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THE

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IN ALL ITS APPLICATIONS TO

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EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CXIV.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2954.—JULY 7, 1916.

BORON:
ITS ABSORPTION AND DISTRIBUTION IN PLANTS AND ITS EFFECT ON GROWTH.*

By F. C. COOK, Physiological Chemist, Bureau of Chemistry.

Introduction.

THE experiments reported in this paper were made in connection with a co-operative study of borax and calcined colemanite as larvicides for the house-fly conducted by the Bureaus of Entomology, Chemistry, and Plant Industry, of the Department of Agriculture. The object of this particular study was to determine the effect of boron-treated horse manure on plant growth, and to study the absorption of boron and its distribution in the roots, stems, and fruit of plants grown on soil fertilised with this manure and on soil fertilised with untreated manure. The plants were grown in pots in the greenhouses of the Department and on open plots at Arlington Experimental Farm, Va.; Dallas, Tex.; Orlando, Fla.; and New Orleans, La. Analyses of the soil from several treated and untreated plots are included. (The writer desires to express his thanks to Mr. W. D. Hunter, of the Bureau of Entomology, for his material assistance in arranging for the experiments in the South).

Certain deposits of boron have been known for centuries, but the wide distribution of this element in mineral and vegetable matter has been recognised only during the last few years. Probably the first to record the presence of boron in plants were Wittstein and Apoiger (14) (reference is made by number to "Literature cited," *prox.*), who found it in the seeds of *Maessa picta*. Since then many observers have found boron in soils, rocks, fruits, and vegetables.

As soils in many places contain boron, it is not surprising that this element is widely distributed in small amounts in plants. It is also probable that boron is present in nearly all animal material. Bertrand and Agulhon (3) report its presence in the hair, horns, bones, liver, and muscles of animals. They detected boron in 27 species of animals, and state that it probably exists in all animals, being more common in those of marine origin. Boron was also found in human, asses', and cows' milk, and in the eggs of the chicken, turkey, and goose.

The toxic effect of boron on plants was first shown in 1876 by Peligot (12), who noted a yellowing of the leaves of beans, and reported that in many cases the yellow leaves fell from the plants. The previous year Heckel (8) reported that 1·25 per cent solutions of alkali borate retarded germination for from one to three days, and that 3 per cent of the alkali borate solutions stopped germination entirely. Loew (10, p 374) states that certain algæ, such as spirogyra and vaucheria, are resistant to the action of boron. Morel (11), however, states that very weak solutions of boric acid arrest the development of lower fungi and similar organisms. He suggests that boric acid may be used, like copper, to attack such diseases as mildew and anthracnose. The effect of boron on the lower plants, fungi, yeasts, &c., has been but little studied.

Agulhon (1) and Bertrand (2) have stated that boron in small amounts acts as a stimulant to plant growth. Pellet (12) calls attention to some experiments which indicate that compounds of both manganese and boron, singly and combined, have no effect on the growth or yield of the sugar-beet. He concludes that the results of other workers claiming a stimulation are too few and are untrustworthy.

Many investigations regarding the effect of boron on plants and plant growth have been reported, but no attempt to review all such experiments is made in this paper. For a review of this subject the publication of Haselhoff (7) and the recent work of Brenchley (4), where various inorganic plant poisons and stimulants are discussed, should be consulted.

Experimental Work.

Very few of the previous studies have included a quantitative estimation of the boron present in plants, and no experiments concerning the effects of calcined colemanite (crude calcium borate) on plant growth have been reported. As both borax and calcined colemanite are valuable larvicides for the house-fly maggot, it seems advisable to determine the effect of manure treated with both borax and calcined colemanite on the growth of a variety of plants.

The manure used in these tests was treated with the amounts of borax or calcined colemanite noted in the tables, and stood in the open for ten days before it was applied to the soil. For the plot tests, the manure was applied at the rate of 20 tons per acre, and was then ploughed under, the ground harrowed, and sometimes rolled and re-harrowed, before planting. In nearly all of these experiments borax or calcined colemanite was applied to the manure in larger quantities than were required to act as a larvicide; *i.e.*, 0·62 per pound per 8 bushels, or 10 cubic feet. When the manure was mixed with the soil at the rate of 20 tons per acre, 216 pounds of borax per acre were present. Furthermore, the manure was not allowed to stand and leach for longer than ten days; consequently, practically the entire amount of borax added reached the soil.

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* *Journal of Agricultural Research*, v., No. 19, Dept. of Agriculture, Washington, D.C.

Table I.—*Percentage of Boron in Wheat and Beets: Greenhouse Pot Tests.*

(Forty parts of soil and one part of boron treated manure were mixed in all the pot and bench tests).

Series No.	Treatment of manure per 8 bushels.	Wheat (dry basis).				Beets (dry basis).			
		Tops.		Roots.		Tops.		Roots.	
		Ash.	Boron as boric acid, ash-free basis.	Ash.	Boron as boric acid, ash-free basis.	Ash.	Boron as boric acid, ash-free basis.	Ash	Boron as boric acid, ash-free basis.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	0·75 pound of calcined colemanite added	15·55	0·0103	20·00	Trace	23·10	0·0315	17·74	0·0020
2.	1·5 pound of calcined colemanite added..	12·96	0·0097	24·76	Trace	21·69	0·0402	12·75	0·0025
3.	1 pound of borax added	12·58	0·0097	33·48	0·0008	22·39	0·0120	14·52	0·0054
4.	1 pound of borax and 1 ounce of lime added	8·51	0·0122	23·39	0·0029	23·07	0·0172	—	0·0097
5.	1 pound of borax and 3 ounces of lime added	9·63	0·0105	25·69	0·0044	22·77	0·0154	14·12	0·0087
6.	1 pound of borax and 9 ounces of lime added	11·07	0·0173	26·24	Trace	20·36	0·0062	14·41	0·0047
7.	Control	9·20	0·0013	23·76	Trace	23·80	Trace	14·56	0·0013

Table II.—*Boron in Tomatoes and Cowpeas: Greenhouse Pot Tests.*

Tomatoes.

Series No.	Treatment of manure per 8 bushels.	Tops.		Roots.		Fruit		Yield of fr .	
		Ash.	Boron as boric acid, ash-free basis.	Ash.	Boron as boric acid, ash-free basis.	Dry matter.	Boron as boric acid, ash-free basis.	No.	Weight.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		Ounces.
1.	0·75 pound of calcined colemanite added..	13·13	0·0054	9·59	Trace	6·04	Faint trace	17	37·25
2.	1·5 pound of calcined colemanite added ..	14·44	0·0107	10·86	"	5·94	"	16	31·5
3.	1 pound of borax added	11·87	0·0146	28·80	None	4·72	"	10	10
4.	1 pound of borax and 1 ounce of lime added	12·95	0·0123	13·76	"	—	—	15	33
5.	1 pound of borax and 3 ounces of lime added	12·15	0·0072	10·66	"	5·26	Faint trace	17	34
6.	1 pound of borax and 9 ounces of lime added	12·00	Trace	19·43	"	5·85	"	18	35
7.	Control	10·12	"	21·88	Trace	5·92	"	23	40·25

Cowpeas (Dry Basis).

Series No.	Treatment of manure per 8 bushels.	Tops.		Roots.		Fruit.	
		Ash.	Boron as boric acid, ash-free basis.	Ash.	Boron as boric acid, ash-free basis.	Ash.	Boron as boric acid, ash-free basis.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	0·75 pound of calcined colemanite added ..	9·27	0·0339	18·52	0·0033	3·68	0·0135
2.	1·5 pound of calcined colemanite added ..	9·25	0·0287	27·04	Trace	3·90	0·0106
3.	1 pound of borax added	8·54	0·0242	24·40	None	3·36	0·0133
4.	1 pound of borax and 1 ounce of lime added	10·96	0·0115	10·01	"	4·12	0·0222
5.	1 pound of borax and 3 ounces of lime added	10·08	0·0237	17·44	"	3·01	0·0097
6.	1 pound of borax and 9 ounces of lime added	11·36	0·0302	20·64	—	3·40	0·0029
7.	Control	7·84	0·0068	22·58	None	3·20	0·0094

Table III.—*Boron in Lettuce and Tomatoes: Greenhouse Bench and Pot Tests.*

Series. No.	Treatment of manure per 8 bushels.	Lettuce (entire plant).		Soluble boron as boric acid in soil on which lettuce was grown.	
		Dry matter.	Boron as boric acid, dry basis.	Upper 6 inches of soil.	Lower 6 inches of soil.
		Per cent.	Per cent.	Per cent.	Per cent.
1.	0·75 pound of borax added..	11·6	0·00036	0·0012	0·0010
2.	1·25 pound of borax added..	10·0	0·00064	0·0022	0·0028
3.	Control	9·0	0·00020	Faint trace	Faint trace
4.	0·5 pound of borax added ..	—	0·00036	—	—
5.	0·62 pound of borax added..	—	0·00042	—	—
6.	0·75 pound of borax added..	—	—	—	—
7.	Control	—	0·00015	—	—

Tomatoes.

Series No.	Treatment of manure per 8 bushels.	Tops (dry basis).		Fruit (fresh basis).		Yield.	
		Ash.	Boron as boric acid, ash-free basis.	Dry matter.	Boron as boric acid, water and ash-free basis.	No.	Weight.
		Per cent.	Per cent.	Per cent.	Per cent.		Ounces.
1.	0·75 pound of borax added	12·98	0·0089	6·55	Faint trace	123	157
2.	1·25 pound of borax added	12·94	0·0196	6·60	"	101	139¾
3.	Control..	10·10	0·0009	6·75	"	120	159½
4.	0·5 pound of borax added..	10·01	0·015	8·10	0·0002	—	—
5.	0·62 pound of borax added	10·77	0·016	8·01	0·0004	—	—
6.	0·75 pound of borax added	7·72	—	7·51	0·0003	—	—
7.	Control	7·72	0·0015	8·00	—	—	—

When 0·62 pound of borax was applied to each 8 bushels of manure and the weight of 8 bushels of manure estimated at 115 pounds (the average weight of fresh manure containing a large amount of straw), 100 pounds of manure contained 0·54 pound of borax, and when the manure was applied to the soil at the rate of 1 part to 40, the percentage of boron in the soil, calculating the weight of 1 acre of soil 6 inches deep as 1,750,000 pounds, was 0·0015.

Tests with tomato (*Lycopersicon esculentum*) and lettuce (*Lactuca sativa*) were made on plants which had been grown in boxes in greenhouses until they were 2 to 3 inches high, when they were transplanted in their respective pots containing the mixtures of manure and soil. The potatoes (*Solanum tuberosum*) tested were of the Green Mountain variety, and the seeds used in growing the other plants were common varieties. The percentages of boric acid as recorded in the tables are calculated to a water and ash-free basis. At least four pots for each treatment were employed in the pot tests. The plots at Arlington Farm were one-twentieth of an acre, and those in the South about one-sixtieth of an acre in size. The tests with lettuce were carried out in benches, each 3 by 5 feet.

Description of Methods.

Many tests for determining boron in foods and other material have been devised. When small amounts are present, as was the case in the present experiments, it is determined colorimetrically, using curcumin, the active principle in turmeric (*Curcuma longa*, L.), a characteristic red colour being given when boron is present.

In preparing the samples the roots were separated from the plants. Both roots and plants were washed, dried, and cut into small pieces for analysis. In some cases the fruit also was tested. In such instances it was washed, dried, and ground for analysis. Boron was determined by the use of freshly prepared strips of curcumin paper, prepared by immersing large unfolded filter-paper in a 0·2 per cent alcoholic solution of curcumin. The procedure was as follows:—About 3 grms. of a dried sample were treated with sufficient saturated lime-water to make the reaction alkaline. After a thorough mixing in platinum dishes the samples were dried and heated in a muffle until all of the organic matter had burned off. Ten cc. of water and a little hydrochloric acid were added, and the solution was warmed, filtered, washed, and made to 100 cc. volume. A 50 cc. aliquot was usually taken for the determination of the boron, but this varied according to the amount present. To the 50 cc. aliquot, or a smaller aliquot diluted to 50 cc., placed in small porcelain evaporating dishes, 2 cc. of hydrochloric acid were added, and strips of curcumin paper were suspended, and allowed to dip into those solutions to the depth of one-fourth of an inch. In all cases standard boric-acid solutions, as well as blanks, were simultaneously employed. After four hours the colours on the strips of paper were compared, and the percentage of boric acid determined.

In the case of soils, the boron soluble in weak hydrochloric acid, not the total boron, was determined. Fifty grms. of soil were shaken with 200 cc. of a solution of hydrochloric acid (1 : 20) for one hour. This was filtered, and 100 cc. of the filtrate made alkaline with lime-water evaporated to dryness, and ashed. The ash was acidified with hydrochloric acid, and the solution made to 100 cc., a 50 cc. aliquot being used for the colorimetric test. In some cases larger amounts of soil were used for the tests. From 2 to 3 grms. of the plant samples were used for moisture and ash determinations. (The analyses were completed with the assistance of Mr. J. B. Wilson, of the Animal Physiological Chemical Laboratory, to whom the writer desires to express his indebtedness).

Results of Experiments.

The results of the experiments are expressed in all the tables and text as percentages of boric acid. Some analyses of boron soluble in weak hydrochloric acid extracts of soils are also reported. The form of the combination of the boron in plants is not known. The boron of soils is in part present in insoluble combinations with silica, and the absence of acid soluble boron in some soils may be thus explained. Ash results are also reported for most of the plants analysed. Separate analyses of the tops, roots, and fruits are tabulated.

In Table I. analyses showing the distribution of ash and boron in the tops and roots of wheat (*Triticum* spp.) and beets (*Beta vulgaris*) three months old, grown in the presence of calcined colemanite and borax, with and without the addition of lime, are recorded. More boron was found in the tops than in the roots of both plants. The beets absorbed more boron than the wheat plants, especially from the soil treated with calcined colemanite. All of the control plants contained a little boron.

A similar series of tests using tomatoes and cowpeas (*Vigna sinensis*) are recorded in Table II. The number and weight of the tomatoes obtained from four pots, which are also recorded, show the injurious action of the boron alone and the benefit derived from adding lime. The tops of the tomatoes contained rather a large quantity of boron, the roots and fruit but traces. More boron was absorbed by the tomato plants when borax was added than with the addition of calcined colemanite. The addition of lime with the borax retarded the absorption of boron. The lowest percentage of dry matter was found in the tomatoes grown on the soil where borax alone was added. The tops of the control plants contained the least ash.

The tops of the cowpeas contained the most boron and the roots the least, the fruit being intermediate. The addition of lime with the borax did not influence the total amount of boron absorbed by the plants. The control cowpeas contained larger amounts of boron than the tomato control plants. The tops of the control cowpeas contained the least ash.

The results of the greenhouse, bench, and pot tests with lettuce and tomatoes are recorded in Table III. It is evident that the lettuce plants took up boron in proportion to the amounts present in the soil. The control lettuce contained the lowest percentage of solids, and indicated the presence of boron. A slight chlorosis of the lettuce plants grown in Series 1 and 2 was seen, but no injury to the roots was observed. The results of the analyses of the upper and lower 6 inches of soil in the benches show an even distribution of the boron.

Tomato plants 1, 2, and 3, Table III., were six months old at the time of analysis. The yield of fruit from three pots in each series, 1, 2, and 3, showed no reduction in the case of the 0·75 pound borax application, but the 1·25 pound borax application reduced the yield. The dry matter of the control fruit, Series 3, is higher than in Series 1 or 2, and the ash of the control tops, Series 3, is lower than the ash for the tops, Series 1 and 2. The tomato plants, Series 4, 5, 6, and 7, were younger and smaller than those of Series 1, 2, and 3. In all the tomato plants (Table III.) the tops contained practically all the boron, the fruit showing only traces.

(To be continued).

NORMAL NONANE.

By LATHAM CLARKE and ROGER ADAMS.

Normal nonane was first synthetically produced by Krafft (*Ber.*, 1882, xv., 1692), by reduction of pelargonic acid, $C_9H_{18}O_2$, with hydriodic acid and phosphorus in a sealed tube heated to 240°. The boiling point at 760 mm. is given by Krafft as 149·5° and the specific gravity, compared to water at 4°, is as follows: 0°, 0·7330; 13·5°, 0·7228; 15°, 0·7217; 20°, 0·7177; 99·1°, 0·6541.

We found the boiling point as 150·4—150·6° at 759 mm. The specific gravity at 15°, compared to water at 15°, is 0·7219. The index of refraction, n_D 25° = 1·4025.

The starting point in the preparation of normal nonane was castor oil. By distillation this yielded oenanthol (normal heptyl aldehyde), which, after purification by means of the bisulphite compound, was treated with ethyl magnesium bromide, giving, after the usual decomposition of the organo-magnesium derivative, ethyl hexyl carbinol, or 3-nonanol. This carbinol was converted into the corresponding carbinol iodide by treatment with iodine and red phosphorus, and the resulting 3-iodononane was boiled with alcoholic potash, which gave nonylene. This last yielded normal nonane on reduction.

Summary.

Castor oil$\rightarrow$
$CH_3CH_2CH_2CH_2CH_2CH_2CHO$, oenanthol$\rightarrow$
$CH_3CH_2CH_2CH_2CH_2CH_2CH(OH)CH_2CH_3$,
3-nonanol$\rightarrow$
$CH_3CH_2CH_2CH_2CH_2CH_2CH(J)CH_2CH_3$,
3-iodononane$\rightarrow$
$CH_3CH_2CH_2CH_2CH_2CH_2CH=CH—CH_3\rightarrow$
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$,
normal nonane.

Experimental.

Oenanthol.—The process used for obtaining oenanthol was a slight modification of the one used by Erlenmeyer (*Ann.* 1875, clxxvi., 342). Five hundred grms. of castor oil were poured into a three-litre flask, which was connected to a condenser containing water in the jacket, but not running water. The flask was placed on a sand bath and strongly heated. A rather rapid distillation of liquid ensued, and the heating was continued until the flow of distillate had considerably slackened, then the burners were removed. The residue in the flask was poured out while still hot. If the heating was continued too long, the residue began to foam badly and became a sort of spongy material, exceedingly hard to remove from the flask.

The distillate was redistilled and a fraction collected between 90° and 180°. This was shaken with a concentrated solution of pure sodium bisulphite and the aldehyde-bisulphite compound crystallised out. This was filtered and pressed out on a clay plate. The best method for the resolution of this into pure normal heptyl aldehyde was to treat with an excess of saturated sodium carbonate solution and distil carefully with steam.

The aldehyde was separated from the water in the distillate, dried over calcium chloride, and redistilled. (Calcium chloride did not have any detectable chemical action on this aldehyde, and was found to be a very efficient drying agent for it). The fraction boiling at 152—157° was that used in subsequent work.

Ethyl-hexyl Carbinol (3-*Nonanol*).—A solution of ethyl magnesium bromide was prepared by dissolving 12 grms. of magnesium in a mixture of 60 grms. of ethyl bromide and twice its volume of absolute ether. To this, 57 grms. of oenanthol in its own volume of absolute ether was gradually added, and the whole allowed to stand several hours at room temperature. The organo-magnesium compound was decomposed in the usual way with water and dilute sulphuric acid. The ether layer containing the carbinol was separated, and dried over potassium carbonate. The ether was then distilled off and the residue fractionated. 45 grms. of carbinol were thus obtained, boiling at 192—193° at 755 mm.

This alcohol has been previously made by Wagner from oenanthol and zinc ethyl (*J. Russ. Chem. Soc.*, xvi., 306), and by Gerard from oenanthol and ethyl magnesium bromide (*Chem. Zentr.*, 1907, i., 1398).

3-*Iodononane.*—This was obtained from 3-nonanol by the usual procedure for the conversion of alcohols into iodides. In a typical experiment 40 grms. of 3-nonanol were mixed with 4 grms. of red phosphorus and 36 grms. of iodide. The mixture, which at first was artificially cooled, was later heated for two hours on the steam bath, then filtered to remove unchanged red phosphorus, washed with water to remove acids of phosphorus, and without further purification was converted into nonylene.

Normal Nonylene.—The above 3-iodononane was refluxed with excess of strong alcoholic potash for about an hour. The liquid in the reaction flask was distilled, and yielded a solution of nonylene and alcohol, these forming a mixture of minimum boiling point. On the addition of much water, the hydrocarbon separated as a floating layer, which was removed, washed with water, dried with calcium chloride, and distilled from metallic sodium. On subsequent fractionation, the main portion boiled at 149·4—149·9°.

Properties.—Colourless liquid, very mobile, pleasant petroleum-like odour. It boils at 149·4—149·9° and has at 15° the specific gravity of 0·7540 compared to water at 15°.

Calculated for C_9H_{18}—C, 85·7; H, 14·3. Found—C, 85·3; H, 14·2.

Normal Nonane.—Normal nonylene was reduced to normal nonane by passing the vapour of the former, together with hydrogen, over freshly reduced nickel at a temperature of 160°. (The exact procedure may be found in an article by Clarke and Biggs, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 59).

Properties.—Colourless, very mobile liquid, with a very slight "sweetish" odour. B. p. 150·4—150·6° at 759 mm. The specific gravity at 15° compared to water at 15° is 0·7219. The index of refraction n_D 25° = 1·4025. It is miscible with the common organic solvents.

Calculated for C_9H_{20}—C, 84·4; H, 15·6. Found—C, 84·1; H, 15·7.

—*Journal of the American Chemical Society*, xxxvii., No. 11.

THE CONTENT, METHOD, AND RESULTS OF THE HIGH SCHOOL COURSE IN CHEMISTRY.*

By ALEXANDER SMITH, Columbia University, New York City.

When, some fourteen years ago, I was writing my half of a book on "The Teaching of Chemistry and Physics" and attempting to collect all the important discussions of the subject, I found in the reports of the New York State Science Teachers' Association more valuable suggestions than in all other sources put together. It gives me especial pleasure, therefore, to meet with so many who are members of that association, and to acknowledge the debt which I owe to their papers, and particularly to the report of the Committee of Nine.

I find that we cannot follow the order of the title, for the *content* may be barren of results if the *method* of using it is not sound, and the methods employed naturally depend upon the *results* which are desired. We begin, therefore, with the results, because they determine the content and the methods.

It is not our aim to begin the training of chemists, although we are proud of such of our pupils as do become chemists. Nor are we preparing our pupils to enter college, for on an average only about 5 per cent of our graduates enter college, and of these perhaps only 25 per cent continue the study of the science there. Our course is thus to a small extent a foundation for more chemistry and to a large extent a part of a general education. It must help the man to sell life insurance or to take part in business as a clerk and work his way into a higher position. It must help the woman to do good office work, to perform household duties intelligently, and to know whether her child has some serious disease or is only imitating some disease while cutting a tooth. It is part of an education for life.

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* Address before the Science Section of the New York State Teachers' Association. From *School Science and Mathematics*, 1916, xvi.

Chemistry Teaching for By-products.

Now, the specific operations of business and of housekeeping are not discussed in the course. Apparently, we must teach three ways of preparing oxygen, five chemical properties of chlorine, six physical properties of hydrogen, and the uses of these substances, in such a way that the process adds to the *general* mental and physical efficiency of the pupil. Evidently, we teach chemistry, in part at least, so as to secure several important *by-products.* After all, the fact that the by-products may be as valuable as the primary product is to the chemist not a new idea. Yet this conclusion reveals the fact that our task is an enormously difficult one. It is easy to take a text and to make the pupils memorise lists of elements, lists of atomic weights, lists of properties, and lists of modes of preparation, but, if the information is simply piled into the memory without plan or connections, it is not a part of a real education. Arranging bricks, according to a plan, so as to produce some useful structure, is one operation, and throwing them into a heap is another and much less useful operation. The methods of extracting the by-products is not shown very conspicuously in the books—the handling of almost any book could be done mechanically and fruitlessly. Not the topics, but the way of handling them, will determine their value. The chemistry must be made largely a means, and not entirely an end in itself.

Live Chemistry.

Now, clearly, chemistry that is to yield valuable by-products must be *alive*—not dead. Let us assume that *live chemistry* is the desired result, and try to define the term suitably. The term seems to be used in different senses. Varnish and photography could be taught so as to be as dead and useless to the young pupil as indium or europium. It is not a question of live subjects; the subjects are not themselves alive, but the method of handling them must be so. Live chemistry must mean chemistry learned so that the pupil is interested in it and becomes more intelligent during the process. This is the result we are striving for. It must be chemistry, or it is not what we are discussing. It must be alive, or it is not education. It must therefore be both.

For our purpose, the analogy of the living plant is suggestive. The living plant is recognised by four characteristics. It is *rooted in the ground*, and its roots and root hairs permeate every part of the soil. They also draw water, with dissolved food (potash, combined nitrogen, &c.), from it. It *spreads its stem and leaves in the air*, and takes in nourishment (carbon dioxide) through these organs. It *grows*, and so demonstrates its successful connection with the soil and the air. It is *useful*, as food if a vegetable, or for ornament if a flowering plant, or for shelter and lumber if a tree. Pull up the plant and it dies. It dies because the connections with the soil and air have been destroyed.

The Chemistry Plant.

Is not live chemistry like a plant? It must be rooted in the pupil's head. That is, to live, it must be intimately related to the previous knowledge and habits of thought of the pupil. It is useless to plant the chemistry away from all the elements of the pupil's previous education and previous acquirements—just as useless as to plant a vegetable two feet above the ground, if we expect it to live. This suggests the idea that a soil analysis of the pupil's brain might be useful to one who intends to plant something new in it. It suggests also that we must select those parts of chemistry which can be related to the previous knowledge, the powers, and the interests of the pupil.

The spreading of the leaves corresponds to the mental and physical environment of the pupil. In Gary he will be interested in steel and metallurgy, in other places in photography or agriculture. In all surroundings he is familiar with many articles and processes which have intimate connections with chemistry. The girl is familiar with cleansing and with materials and processes used in the house. Discussions of the applications of chemistry will thus contribute to the intellectual nourishment of the pupil.

Again, the chemistry, like the plant, must grow. Merely memorised chemistry will lie largely unaltered in the mind. We must not plant bare chemical results, any more than we would plant full-grown cabbages. We must plant ideas, and we must establish connections between them and the previous knowledge (the soil) on the one hand, and the practical applications (environment) on the other.

Finally, the chemistry plant must be useful. Amongst plants, it resembles the legumes (clover, alfalfa, &c.) more than any other family. The chemistry crop must be of value in itself, but, more than this, it is our hope that it will fertilise the soil and enable this to produce still better crops of other kinds later. We must improve the pupil's habits of thought, and give him, if possible, tendencies to correct observation and reasoning, mental flexibility, and initiative.

A Soil Analysis.

Clearly, the soil, that is, the previous knowledge, experience, and mental habits of the pupil, must be studied and analysed. We soon discover that there are two kinds: the kind we imagined occupied the pupil's head, and the kind that is actually there. For example, we know that the pupil has had all the rules of arithmetic, and we assume that he will readily apply them in chemistry. Often the pupil has had physics, so we assume that it will not be necessary to teach him anything about that science, and we expect that he will apply his knowledge wherever possible. We assume that he has some practical knowledge, and will not try to boil water in a thick-walled glass bottle. When we find he has successfully set up an apparatus to generate hydrogen, but on closer inspection discover that he has used glass rods throughout, instead of tubing, we become more awake to the actual situation. The pupil has had so much training in language work, and especially in English, that we expect him to use words with discrimination, and to describe his observations with precision. But he calls a bead "clear" when he means colourless, forgetting that it might be clear and also blue (like the clear blue sea) at the same time. Finally, we discover that, to secure clarification of his rambling statements, we must teach him the technical vocabulary of chemistry as if it were a lesson in a language, and demonstrate to him anew that clear expression is necessary to clear thinking.

But there have been still other farmers working in the same soil before our turn came. Did the teachers of mathematics, Latin, French, and history put into the soil anything that we can use? In studying a foreign language we meet a new word, and the dictionary gives three English equivalents, often all more or less obsolete words. We obtain only a hazy notion of the meaning. But we meet the same foreign word again and again, in new connections, and each time we gain a clearer idea of its usual meaning. We compare the cases, we make hypotheses in regard to the meaning, and we adjust each hypothesis until we reach certain knowledge. Thus, by repeated observation and comparison, and by the construction of hypotheses, we ascertain the facts. Is not this the scientific method? Perhaps we assume that the use of this common-sense method is natural. In reality, however, it is an acquired habit. Do we believe that the supposed cure for the plague, by hanging a spider in a bag round a man's neck, was ascertained by trying different animals until the spider was selected, and different species of spiders until the one that effected a cure was discovered? On the contrary, we know that a striking, perhaps, repulsive notion will be accepted by the average human being, without any evidence, much more readily than a well-studied but less exciting statement. The scientific habit of mind has to be acquired by constant self-restraint, and constant practice.

Some think that the study of a language is mere memory work. But many words have several different meanings, and observation and reasoning must be employed in ascertaining the meaning in any given case. Take the word hold. We can hold (own) stock. We can hold (arrange) a meeting. A vessel can hold (contain) water. We can hold (maintain) a course. One can hold one's tongue, where hold means to withhold, or one can hold a conversation, where it means just the opposite. One can hold (judge) another man to be a fool, and one can hold forth on the teaching of chemistry. In languages, things which are equal to the same thing are not equal to one another, and the use of the scientific method in finding the true meaning in a given case is indispensable. Then, too, there are generalisations or laws in languages. Like natural laws, each states some general fact, and is called a rule of grammar. In language work, experiments are frowned upon, but the other features of the scientific method are in continual use. We may assume, therefore, that the pupil has learned the scientific method, and that he can and will apply it. All this is the analysis of the soil as we imagine it.

Sometimes we go further. Prof. Hall tells of a teacher of physics who placed a block of wood before each pupil, and expected each to draw a conclusion. After an interval of severe strain, the visitor asked the teacher what conclusion he expected them to draw? "Why," he said, "the conclusion that matter will not set itself in motion of its own accord." The pupils were expected to invent the conception of inertia!

While enumerating the constituents of the pupil's previous knowledge, such as arithmetic, physics, and the scientific method, we realise that they must form an excellent soil for the growth of live chemistry. But, after some experience as teachers, we discover, also, that connections with these valuable elements are not made spontaneously by the pupil. Unless we assist the pupil in making the connections, the fertile materials might as well not be there. Shall we decide that we have no time to make the connections; that we are there to instil a lot of chemistry, and have no concern with whether it lives after being planted? What should we think of a farmer who said "I am here to dig potatoes and sell them, not to spend months in planting and hoeing"; or, "I wish to cut corn, or to pick cotton, and sell it, not to labour over the raising of a crop"? We should know in advance that he was bound to fail.

New Applications of Arithmetic Hard to Make.

The pupil has had arithmetic, but he has applied it to apples and bricks and ditches. A new application, to chemistry, is confusing. The human mind works in ruts far more than we realise. Tell a man the uses of the various levers employed in running an auto, and he will believe he could run it. But let him try, and he will discover his mistake. He opens the throttle when he intended to throw out the clutch, and before long he does three wrong things all at once and stalls the engine. After an hour's practice, he is thoroughly exhausted in mind and body. Yet he had to do no one thing that required effort, or was in itself very novel. It was the new combination of purposes and motions that floored him. If I were to give you a problem in chemical arithmetic, you would find it easy. You would perhaps think you were reasoning it all out from abstract principles. In point of fact, however, being familiar with that sort of problem, you would have from the start a general view of the stages in the operation and of the result to be expected, which would be of great assistance. For the rest, you would follow routine methods acquired by habit, and of genuine, pure reasoning there would be very little. Let me rather give you a proposition in arithmetic applied to zoology. In this connection you, as teachers of chemistry, have no preformed, semi-blind habits, and you have to depend on reasoning. Also, you cannot focus the answer itself more or less clearly before the working begins. The problem will therefore be more like a chemical problem set before a novice in that science. The proposition is that, if there are more cows in the world than there are hairs in any cow's tail, then there must be at least two cows in the world with the same number of hairs in their tails! A chemist cannot even grasp the proposition, much less recognise its truth. He cannot recall whether it stated that there were more hairs or more tails, or more cows in the world. Suppose the proposition had been: If there are more atoms in the world than there are different atomic weights, then there must be at least two atoms with the same atomic weight. Any teacher of chemistry can see that to be true. He thinks he has verified its truth by reasoning. In point of fact, however, he knows in advance that there are innumerable atoms of each of the ninety kinds, so he can accept the conclusion without having to reason it out at all. The pupil has not this advantage, and so stumbles pitifully. Even after this chemical parallel, the chemist cannot see through the cow problem. Zoological arithmetic requires reasoning, of a chemist, and none of us reason until compelled to do so.

Being teachers, however, we know where the trouble lies. A general statement is always apt to be confusing, so we skilfully substitute simple, concrete numbers for the x's and y's it contains. Suppose there are only *four* cows. Now, "there are more cows in the world than there are hairs in any cow's tail." That permits the hairiest cow to have three hairs in its tail. The second has two hairs. The third has one hair. The fourth cow *must*, therefore, repeat one of these numbers. Hence, if there are more cows in the world than there are hairs in any cow's tail, there must be at least two cows with the same number of hairs in their tails!

If the fourth happened to be a Mexican, hairless cow, the proposition would have to be restated, so as to cover that possibility. To restate it will place serious mental strain on a chemist—although a zoologist can do it without effort.

The teacher needs to realise afresh every year how difficult and confusing a subject, old to him, but new to his pupils, can be. Perhaps if he were to spend a part of every summer, learning to play some simple musical instrument, he might begin the year with a more vivid recollection of the nnmber of blunders an intelligent person can make in doing something demanding a little thought and the acquirement of new habits. We expect of our pupils a mental and physical alertness and adaptability which we are far from possessing ourselves.

Applying the Scientific Method.

Our pupils have been using the scientific method, but they are not masters of its use. How few investigators, even, can use it outside the limited range to which they are accustomed. Cavendish, as a chemist, was unusually able. But, when his housekeeper asked him what he wanted for dinner, he used the scientific method, and finally said, "A leg of lamb." He never noticed that every time the question was asked, he always reached (by reasoning?) the same conclusion. When two eminent Frenchmen were coming to dinner, the housekeeper ventured to hint that something more than usual would be desirable. Rigid and prolonged application of the scientific method led finally to the reply: "Yes, let us have two legs of lamb." Yet, his reasoning about the gases in the atmosphere was admirable, and, if the spectroscope had been known in his time, he would have advanced the date of the discovery of argon by a hundred years.

The pupil's use of the scientific method in language study was entirely unconscious. How, then, can we expec him consciously to apply it to chemistry? It is there, in his mental soil. But, like the potash in felspar, it is in chemical combination with other things, and has either to be set free with the help of the teacher, or be introduced in the form of a fresh supply, before it becomes available to the chemistry plant. In one college physical laboratory, the directions for an experiment were to take a gauge and measure the diameter of a wire in several places. The instructor assumed that the pupil had learned the value of repetition in previous studies, and knew why it was of value. But one pupil came up and said: "I have measured the diameter of the wire in all the four corners of the room. Where shall I measure it next?" The same pupil had probably met the word *cum* hundreds of times. But, instead of realising that this repetition was responsible for his very precise knowledge of its meaning, he simply thought that it was an unusually nice word, because, after five or six encounters, he was no longer compelled to look it up in the dictionary.

Then, too, while fact, and hypothesis, and law are used in language work, they are not so named in that connection, and their identity when again encountered in chemistry is not recognised. Still, again, the phenomena of the language are in print, and all the pupils are observing the very same phenomena. Counting and classifying the appendages of the cockroach is not very difficult, if every pupil is supplied with a specimen. But when, as in chemistry, each pupil has to create for himself the phenomena to be observed, it is no wonder that variations arise and that reasoning from different data leads to divergent conclusions. Chemistry is like language study, only it is much more difficult, and we must not expect our pupils to be geniuses. The most minute subdivision of the steps in reasoning and the most sympathetic assistance are required, if any rational elements are to enter into the process of learning chemistry.

In view of the difficulties connected with the use of the scientific method, is it worth while to try to bring it to the notice of our pupils? Assuredly it is. How does the successful business man proceed? He gathers all the information he can. He analyses the apparent facts and classifies them. He finds some which are not facts, some which are only half-facts, some which go far beyond the facts (exaggerations), and some which, although true, are side issues and present a distorted view of the situation. Finally, he ascertains the exact nature of the problem, and proceeds to devise means to meet it. The scientific method is here called business-sense. Like the same method in languages, its use is largely unconscious. But, in its absence, failure or subordination and mediocrity are certain to be the results. The physician in his diagnosis, and the lawyer in trying to convince a judge or jury, use the same method. Our hope is that, after using the method in languages, chemistry, biology, and other studies, the pupil may acquire some slight tendency to use the method, after graduation, on the problems of life. We expect nothing wonderful, but we hope for some result of this nature. If only we can produce a little awakening, so that the value of rational methods dawns on the pupil, we may be sure that later the fierce interest in his business and the keen competition of others will urge him along the right track and enable him to develop himself into a useful and successful citizen. Is not this a by-product from the course in chemistry which is worth striving for? It may be our particular privilege to strike the spark, where other teachers have tried and failed, and so, to change the metaphor, to inoculate the pupil with the germ, which will later determine his development as a leader rather than an underling. Surely, chemistry, taught with a view to such results, must be live chemistry.

Applications Essential to Live Chemistry.

Besides being rooted, a living plant must be in intimate, extensive contact with the air. Just so, the course in living chemistry must be not only in close relation with the mental soil, but it must also be in contact with surrounding chemical phenomena and materials. Relations with applications of chemistry are essential. The atmosphere of everyday life is full of possible contacts with chemistry, and all the teacher has to do is to make the connections. The essential thing, however, is that the applications must be connected with the chemistry in a *vital* fashion, if the plant is to be alive. Some applications may be worth memorising, if they cannot be connected intimately with the elementary aspects of the science. But numerous applications which are exclusively or largely of this kind are necessarily dead. They resemble placing a plant in a vacuum, and offering it a brick, when it requires carbon dioxide as food. Aluminium silicate is a perfectly good chemical substance, but it cannot be related through the leaves to the life of the plant. As one reads the lists of "live topics" that have recently been suggested, one feels that memorising must be contemplated, for effecting explicit and vital contact between them and the elements of chemistry is beyond the powers of the great majority of teachers. Tests for adulterants in oils and honey can easily be used, mechanically, but can they all be explained and used to give life to the chemistry in the time available—or at all? Clay and its products are important, but there are acid salts much simpler in composition and easier to utilise as educational material. Cement and glass are of immense importance, but is the laboratory equipped for the optical and physico-chemical study of cement and its reactions? New stunts in photography somehow suggest an appeal to the emotions, rather than to the mind as a rational organ. The applications are a valuable supplement to the more systematic chemistry, but should not play the part of a substitute for it. Such a substitution would kill the chemistry.

A recent suggested examination syllabus of applied chemistry contains nothing about lead excepting, "Lead pipe and shot — Lead poisoning." Lead pipe is a question of engineering. Lead poisoning is a biochemical item of profound difficulty, if it is to be handled so as to bring out the instructive details. Further on we find "Household disinfectants; hydrogen peroxide, hypochlorites, carbolic acid, mercuric chloride, formaldehyde." No mode of preparation, chemical reaction, or property of any of the substances is called for, and therefore the examiner would not dare to set a question demanding an answer on these points. Is it proposed to have the pupils prepare media, cultivate pathogenic bacteria, and observe the behaviour of organisms in presence of these disinfectants? Microscopes and sterilising apparatus would be required, and there would be serious danger of infections and illness. This kind of live chemistry might kill some of the pupils. Apparently it is merely a question of memorising the words, for nothing else that is practicable is called for.

(Note.—Disinfecting power is not a chemical property, although often given as if it were. Hydrogen peroxide kills by oxidising, and so do hypochlorites, but formaldehyde is a reducing agent. The chemical property in the first two cases is that the substance is an oxidising agent. The disinfecting is an *application* of this property. Again, bleaching powder is often given as a chemical property of hypochlorous acid. But the chemical properties are, that hypochlorous acid is an oxidising agent; sodium hyposulphite, a reducing agent (bleaches indigo in the dye vat), and sodium hydroxide, a base (bleaches blue prints). Each of these substances can be used for bleaching, but the bleaching is an application of one of the chemical properties named, and is not itself a chemical property. Chemical properties must be stated so as to indicate some type of chemical reaction).

Applications suitable for live chemistry must be related to the previous knowledge of the pupil, and to his surroundings. They must not be related solely to his curiosity. As a rule, they must be selected so as to be capable of experimental relation to the elements of the science. It is not sufficient that they attract the attention of the pupil. They must explicity require utilisation of this attention for educational purposes. It is a question—as in the case of a plant—of *relating* the chemistry to the environment and *vice versa*. The items suggested are often such as, with nine teachers out of ten, could only be placed, unrelated into the memory of the pupil, there to be found undigested and unused, as an inert deposit, at some later date.

The Content.

So much has been said, indirectly, about the content, that little need be added; almost any of the current selections will serve the purpose, provided it deals with chemistry, and provided it affords the possibility of intimate relations with previous knowledge and with familiar phenomena and applications.

(To be continued).

THE SCOTTISH SHALE OIL COMPANIES.

A SUCCESSFUL year has been had by the Scottish Shale Oil Companies, notwithstanding that advance contracts prevented them from deriving the full benefit from the higher prices. The aggregate profits of the four leading companies — Pumpherston (incorporating Tarbrax), Young's Paraffin Light and Oil, Broxburn, and Oakbank (incorporating Dalmeny), amounts this year to £301,413, including balances brought forward, and for the previous year £175,239.

The policy pursued by the companies is the laying up reserve funds and creating large sums for improved plant and extensions of refineries and mines, in addition to writing off considerable amounts for depreciation. New plant has been introduced into all the works with the object of economising labour, increasing output, and utilising to the last degree all waste. The revenue from by-products is increasing, and the latest processes are adopted to add to the yield per ton of shale. New plants installed in oilworks include a complete vitriol plant at the Addiewell Works of Young's, and a caustic soda producing plant at Broxburn Works only just erected and placed in working order.

Extensions of shale fields are being carefully engineered. The Oakbank Company have leased from the Crown valuable fields of shale under the sea-bed of the Firth of Forth and intend to secure a good output of shale to add to the supply from their existing fields at Deans, Westwood, and Dalmeny. Electric generating stations for the central works of the companies are now in active order and supply power for all purposes both under and on the surface. The Pumpherston and Broxburn electric power houses are of large size and can work up to high power. The Pumpherston Company have not only paid off for the past year £5156, expenditure on improved plant, but have credited £20,000 to the improved plant account to pay future developments when these can be introduced; while Broxburn are crediting £5000 to retort renewal account; and Young's Company place £9747 for outlay on new and latest patented plant, including fuel economisers and gas producers. New retorts are installed by all the companies, who have paid particular attention to this department, and where possible older benches of retorts have been modernised with the best possible results as regards production.

All oils and by-products are strongly in demand. Naphtha and motor spirit command the best market price, and Scotch burning oils sell in preference to imported brands. Gas enriching oil is in request, also lubricating oils. Wax and candles are now bringing in the full advantage of the higher market quotations. Sulphate of ammonia is a strong dividend-earning product of the Shale Oil Works. The Board of Agriculture stopped exports in the spring, but since then large consignments have been shipped abroad, and the price now quoted is a remunerative one and considerably in excess of that ruling two years ago. The Scotch companies have their selling prices determined by their central organisation at Glasgow, and these are governed by the quotations of foreign importers. Although all rates of materials are up—whether for refineries, workshops, or mines—also wages, yet the prices now ruling, together with the improved processes at the works, enable the companies to face competition successfully and to write off large sums for depreciation, the amount placed to depreciation by Young's this year being £20,000, by Broxburn £16,194, and by Pumpherston £15,000. Dividends paid on the ordinary shares would have been better but for various circumstances, one being the contracting at comparatively low prices for wax and candles for months ahead, the other earlier difficulties with employees. Young's, owing to fire at the Addiewell Works last autumn, are paying no dividend on the ordinary shares this year, although financially they are in a strong position; Pumpherston declare 25 per cent, as compared with 10 per cent the previous year; Oakbank give 10 per cent; and Broxburn 7½ per cent, no dividend being paid on the ordinary shares on the former balance-sheet. Future prospects are good, and the companies now can benefit to the full from the very large outlays on improvements and extensions and the important developments they have brought into force during the past few years.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 22, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE CROONIAN LECTURE was delivered by Prof. S. J. HICKSON, F.R.S., on "*Evolution and Symmetry in the Order of the Sea-pens.*"

In the animal kingdom two dominant types of body symmetry are to be found. In animals that are sedentary or floating in habit the symmetry is frequently radial, but in animals that are free and move rapidly by their own muscular activity the symmetry is bilateral. In those classes of animals now sedentary in habit, which by their developmental history show a descent from a previously free and bilaterally symmetrical ancestry, a secondary radial symmetry is usually found either in the form of the body or in the arrangement of the organs for the capture of food. Similarly, in the Echinodermata some examples are found, particularly in the class Holothuroidea, of animals descended from a sedentary and radially symmetrical ancestry assuming with their freedom and increased muscular activity a secondary bilateral symmetry.

In the groups of animals that are radially symmetrical whether sedentary or floating in habit, there is usually a far greater range of variability than in those that are bilaterally symmetrical, and in the endeavour to classify them in genera and species on the Linnæan system the zoologist finds so many cases of overlapping and fusion that some doubt arises as to the existence in Nature of discontinuous specific groups.

In the order of the sea-pens there is a complete series of forms connecting the radially symmetrical colonies of the genera Veretillum and Cavernularia with the bilaterally symmetrical genera Pennatula and Pterœides. In this series the difference between the range of variation in the radially symmetrical genera and that in the bilaterally symmetrical genera is very pronounced.

In such characters as the size of the zooids the size and shape of the spicules, the length of the axis, remarkable variations are found in the radially symmetrical genera. In the bilaterally symmetrical genera these characters are far more definitely fixed, and can usually be relied upon for determination of species.

Having examined a large number of specimens of the

Pennatulacea collected by the Siboga Expedition and in other collections in this country and abroad, the author believes that in some of the radially symmetrical genera there is no such discontinuity of structure as would justify their division into specific groups. In the bilaterally symmetrical genera, on the other hand, the existence of definite specific groups is certain. If this view is justified, the conclusion would be reached that the evolution of those discontinuous groups of specimens which are commonly recognised as species is correlated with the change from a radially symmetrical to a bilateral symmetry of the body.

The evidence at present at our disposal points very definitely to the conclusion that the radially symmetrical sea-pens are more primitive than the bilaterally symmetrical sea-pens, and evidence is produced which suggests that the former are derived from an Alcyonacean ancestry which assumed a floating or drifting habit.

PHYSICAL SOCIETY.

Ordinary Meeting, June 16, 1916.

Prof. G. W. O. Howe, D.Sc., in the Chair.

A paper, entitled "*Experiments with Mercury Jet Interrupters*," was read by Capt. C. E. S. Phillips.

The paper describes an experimental attempt to ascertain the form of the mercury column issuing from a hole in the side of a rotating drum, that is continuously supplied with mercury by centrifugal action.

Incidentally, a new form of interrupter is introduced, in which the interior is visible through a window in the lid. The arrangement forms a suitable apparatus for experiments with various forms of orifices and metallic contact segments, and the paper gives an account of work in that direction. As it is important to ensure the cleanliness of the mercury in interrupters of this type, the usual copper segments are replaced by ones made of tantalum, which for many reasons is preferable. It is not "wetted" by mercury, it remains clean and bright indefinitely, and its high melting-point renders it lasting.

Experiments with various forms of orifice are described, and it is pointed out that the issuing stream is only slightly affected by this means. An explanation is given of the fact that a vertical slit orifice will not produce a ribbon of mercury, and that no matter how much the diameter of the orifice is increased beyond about 2 mm., the cross section of the mercury column remains unaltered. A method is described, however, by which a much larger stream of mercury can be obtained from the rotating drum, if necessary.

Brief reference is made to experiments with various volatile liquids in suppressing the flare which occurs when the mercury columns leave the contact segments. The three well-known substances which are most effective in this respect are coal gas, hydrogen, and ether.

It is pointed out that experiments of this nature are necessary, in view of the wide use now made of mercury interrupters in X-ray work.

Discussion.

Capt. Reid thought the instrument described by the author was of considerable importance. In practice it would be a great advantage to see the interior of the instrument when anything went wrong.

Dr. R. S. Willows congratulated Capt. Phillips on having broken new ground in his experiments. Mercury interrupters had not been very scientifically investigated so far. He thought experiments on the thickness and resistance of the jet, on the resistance at the contact with the tantalum vane, and on the effect of varying the inductance of the primary circuit on the performance of the interrupter, would yield results of importance. Had the best shape and inclination of the plate on which the jet impinged been worked out? With regard to the effect of different gases in quenching the flare, he thought the specific inductive capacities were the determining factor rather than the specific heats. The same problem was met with in running a singing arc.

Mr. G. L. Addenbrooke mentioned that one firm he knew of made interrupters with an electrode of variable inclination.

Capt. Phillips, in reply, said that some of the points raised by Dr. Willows were dealt with more fully in the paper than in his description. The resistance of the jet was a very interesting point, and he had some experiments in progress on the matter. He was not quite clear whether the seat of the resistance was the mercury column or the junction of the column with the electrode. The position of the electrodes was also dealt with in the paper.

A paper, entitled "*A Method of Measuring the Pressure of Light by means of Thin Metal Foil*" (Part II.), was read by Mr. G. D. West.

The pressure of the radiation emitted by a carbon filament lamp, at a distance of a few cm., is sufficient to cause a microscopically measurable deflection of the end of a strip of gold or aluminium foil, suspended in a closed test-tube. By this means the radiation pressure may be measured, and the results may be checked by a comparison with the energy density of the radiation, as deduced from the initial rate of rise of temperature of an exposed blackened copper plate.

In a previous paper, experiments were carried out in atmospheres of air and hydrogen, and at pressures extending from 76 cm. to 1 cm. of mercury. Under certain conditions it was found possible to obtain satisfactory results. The present paper deals with experiments at pressures from 1 cm. of mercury down to the highest exhaustions that could be reached.

As the pressure is lowered, certain gas-action effects make their appearance, but, inasmuch as there is no appreciable difference of temperature on the two sides of the strip, the effects are somewhat different from those that occur in the ordinary type of Crookes's radiometer.

When the surface of the strip is closer to one side of the containing vessel than to the opposite side, a deflection away from the closer side occurs, and the direction of this deflection is independent of the side of the strip on which the radiation falls. With a symmetrically placed strip the deflection should be negligibly small. An explanation of these effects is suggested in the paper, and a special type of radiometer is described.

The nature of the residual gas in the tube does not seem to be very important material, but it is found that the repulsive force acting on the strip increases with decreasing pressure, until a maximum is reached at about 0·002 cm. of mercury. With further reduction of pressure a progressive decrease takes place.

By symmetrical suspension, and by the use of liquid air and charcoal, it is possible so to reduce the gas action effect that measurements of the pressure of light of reasonable accuracy are again possible.

Experiments on the pressure of light may thus be advantageously carried out at the highest vacua obtainable, or at pressures as far above 0·002 cm. of mercury as convection currents will permit. The latter alternative is the easier and leads to more consistent results.

A paper, entitled "*The Viscosity of Suspensions of Rigid Particles at different Rates of Shear*," by Edith Humphrey, B.Sc., Ph.D., and Emil Hatschek, was read by the former.

This investigation was undertaken with a view to testing the Einstein-Hatschek formula at variable rates of shear. According to this formula the viscosity of a suspension of rigid spherical particles grows in linear ratio with the aggregate volume of suspended particles, and is independent of their size, as long as the latter conforms to Stokes's formula.

The suspension chosen was one of rice starch of 0·003 mm., and less, diameter, in a mixture of carbon tetra chloride and toluene having the same specific gravity. The measurements were carried out in a modification of Couette's apparatus, in which the deflection of a cylinder, suspended coaxially in another cylinder filled with the liquid and rotated at different speeds, is measured. All measurements were carried out at speeds below that at which turbulence sets in, so that the deflection was proportional to the product of viscosity × angular velocity.

The results of the investigation are:—(1) The viscosity of a suspension is a function of the rate of shear, and increases as the latter decreases, the difference being more marked at higher concentrations; (2) for all rates of shear the viscosity of the suspension increases more rapidly than the aggregate volume of suspended matter; (3) for any one rate of shear the relative viscosity of a suspension, *i.e.*, its absolute viscosity divided by the absolute viscosity of the medium at the same rate of shear, also increases more rapidly than the percentage of suspended matter, the divergence from the linear increase demanded by the formula becoming less as the rate of shear becomes greater, so that a linear law may possibly hold good at rates of shear higher than those attainable in the present apparatus without turbulence.

The general conclusion is that the assumption on which the Einstein-Hatschek formula is based, viz., non-interference between adjoining particles, is not tenable in the case of suspensions containing between 2 and 6 per cent of suspended matter.

A paper, entitled "*A Correction of some Work on Diffusion by Dr. A. Griffiths and Others*," by Dr. A. Griffiths, was taken as read on account of the lateness of the hour.

When salt diffuses through water, in general there must be a movement of the water due to volume-changes associated with variations in concentration. In the papers to which the recalculation refers reference was made to the velocity of the liquid or solution; but what was meant by the velocity of the liquid was not explained. The author now deals with the velocity of the water-component of the solution, to which a clear mathematical meaning can be given. When salt leaves a given section of the vessel containing the solution, the diminution in volume of the contained liquid is prevented by the automatic addition of water, and of water only. In the papers to which the recalculation refers, the error was made of assuming that the diminution of volume was prevented by the automatic addition of solution. The results by the method of diffusive convection require no recalculation, and agree with Mr. Clack's recalculated values to less than 1 per cent. There is no doubt that the results, as recalculated, given by the three methods employed in the author's laboratory agree within the limits of experimental error, and the author's opinion is that the true value of the coefficient of diffusion lies close to those given by his convective method and by Mr. Clack's gravitational method.

CHEMICAL SOCIETY.

Dr. Alexander Scott, M.A., F.R.S., President, in the Chair.

Ordinary Meeting, June 1, 1916.

The President referred to the loss sustained by the Society through the death on May 18 of Mr. William Washington Houlder, Southall.

The President announced that provisional arrangements had been made to hold the adjourned Extraordinary General Meeting on Wednesday, June 21, at 8 p.m., and that further details would be circulated to Fellows during the ensuing week.

Mr. H. C. Greenwood was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Satish Chandra Banerji, L.M.S., 10/2, Michael Dutt Street, Kidderpore, Calcutta, India; Robert Smith Jackson, c/o Messrs. Kemp and Co., Ltd., Bombay, India; Albert Theodore Kremers, 97, Clarendon Road, Putney, S.W.; and Burrows Moore, B.Sc., 105, Breakspears Road, Brockley, S.E.

The following papers were read:—

"Hydrates of Aluminium Nitrate." By R. Seligman and P. Williams.

"A Cyclic Theory of the Constitution of Metallammines and of Ferro- and Ferri-cyanides." By J. A. N. Friend.

Ordinary Meeting, June 15, 1916.

The President referred to the loss sustained by the Society through the death on May 25 of Mr. Walter Edward Koch.

The President announced that the adjourned Extraordinary General Meeting would be held on Wednesday. June 21, at 8 p.m., in the Theatre of the Civil Service Commission.

Messrs. C. H. Rogers and E. Owen Jones were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Henry Vin Arny, Ph.D., Columbia University, New York, U.S.A; Harry Hey, 59, Fyano Street, South Geelong, Victoria, Australia; and Thomas Needham, 24, Clarendon Court, N.W.

Messrs. A. F. Joseph and J. C. Withers were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Ganesh Sakharan Agashe, M.A., M.Sc.; George Arthur Alder; Frederick Hartridge Branson; Joseph George Clark; Percy Herbert Clifford; John Harbourne Cooke, B.A.; George Van Barneveld Gilmour, B.Sc; Samuel Harold Green; Thomas Bertram Henderson; Frederick William Jackson, B.Sc.; George James; Peter Petrovitsch Lasazeff; Frank Charles Laxton; Frederick Owen; Maurice Ernest Probert; William George Ramsay, B.Sc.; Simon Solomon; Fred Taylor; Cecil Francis Tidman, B.Sc.; Arthur Rokeby Ward; William Alexander Whitton, B.Sc.; and David Christophorovitsch Zavriew.

The following papers were read:—

"Studies on the Walden Inversion. Part IV. The Kinetics and Dissociation Constant of Phenylbromoacetic Acid." By G. Senter and S. H. Tucker.

"Reactivity of the Halogens in Organic Compounds. Part IX. Interaction of Alkalis and Alkali Bromoacetates and Bromopopionates in Ethyl Alcoholic Solution." By G. Senter and H. Wood.

Adjourned Extraordinary General Meeting, June 21, 1916.

The President referred to the notice summoning the meeting that had been issued to Fellows. Each Fellow had been invited to state which of the three following proposals most nearly expressed his opinion with regard to the question of the removal of the names of alien enemies from the roll of Honorary and Foreign Members:—

(1) Unconditional removal of the names.

(2) Retention of the names with suspension of judgment until after the war.

(3) Adoption of the following resolution:—

> That the Fellows of the Chemical Society hereby record their detestation of German malpractices in connection with the war, and whilst they refrain at the present time from attaching personal responsibilty for the initiation of these to individual chemists, they desire to mark their protest by resolving that the names of the following alien enemies—A. von Bayer, T. Curtius, E. Fischer, C. Graebe, P. H. R. von Groth, W. Nernst, W. Ostwald, O. Wallach, and R. Willstätter—shall not appear in the list of Honorary

and Foreign Members so long as the war shall last, after which their position shall be reconsidered.

Of the 3221 notices issued to Fellows 1266 replies were returned, and of these 18 were ineffective. The opinions as recorded in the remaining 1248 papers were as follows:—

For Proposal No. 1	471
" " " 2	295
" " " 3	482
	1248

The President stated that the motion before the meeting was:—

> That judgment be suspended until after the war, in accordance with the resolution of the former Council.

Mr. Julian L. Baker moved as an amendment to this motion:—

> That the Fellows of the Chemical Society hereby record their detestation of German malpractices in connection with the war, and whilst they refrain at the present time from attaching personal responsibility for the initiation of these to individual chemists, they desire to mark their protest by resolving that the names of the following alien enemies—A. von Baeyer, T. Curtius, E. Fischer, C. Graebe, P. H. R. von Groth, W. Nernst, W. Ostwald, O. Wallach, and R. Willstätter—shall not appear in the list of Honorary and Foreign Members so long as the war shall last, after which their position shall be reconsidered.

This was seconded by Mr. F. F. Renwick, and after considerable discussion it wss put to the meeting and was declared lost.

A second amendment to the motion was then proposed by Mr. J. Hodgkin in the following terms:—

> The Chemical Society considers that it is neither compatible nor consistent with its loyalty to the Crown, whence the Royal Charter under which it works was derived, to retain any alien enemies upon its List of Honorary and Foreign Members.
>
> It is therefore resolved that the names of A. von Baeyer, T. Curtius, E. Fischer, C. Graebe, P. H. R. von Groth, W. Nernst, W. Ostwald, O. Wallach, and R. Willstätter, who were elected under happier conditions in recognition of their eminent services to chemical science, for which the Society still retains an undiminished appreciation and regard, be, and are hereby removed from the List of Honorary and Foreign Members.

This was seconded by Dr. S. Russell Wells, and after being put to the vote was declared by the President as carried by 94 votes to 76.

It was then put as a substantive motion and carried.

NOTICES OF BOOKS.

The Respiratory Exchange of Animals and Man. By August Krogh, Ph.D. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1916. Pp. viii.+173. Price 6s. net.

This monograph deals with the quantitative aspect of the catabolic activity of the living organism, and while not attempting to give an exhaustive account of the subject provides an excellent outline of the essentials of the methods of investigation employed and a well-balanced summary of the chief results which have been reached. The methods of measuring the respiratory exchange which have been worked out by various investigators are classified and fully described, and some attention is paid to the exchange of nitrogen, hydrogen, methane, ammonia, and other gases of minor importance. The facts that have been accumulated are then very carefully reviewed, the variation of the standard metabolism under the influence of internal and external factors being first considered. A great number of experiments on the influence of temperature and other physical conditions are fully described, and the alteration of metabolism during the life of the individual and the differences observed in different species are also discussed. The author may be congratulated upon having produced a useful summary of a branch of chemical physiology in which a compilation in the English language was really needed.

Alfred Russel Wallace: Letters and Reminiscences. By James Marchant. In Two Volumes. London, New York, Toronto, and Melbourne: Cassell and Co., Ltd. 1916. Pp. xi.+320; 291. Price 25s. net.

Many an hour's delighful recreation lies before the readers of this book when they first open its pages, and it is perhaps not too rash to prophesy that many duties will be neglected because of the exceeding difficulty of desisting when once one has begun to glean from it. It is a book to be bought and read again and again, for it contains an extraordinarily sympathetic analysis of a personality of the most conspicuous charm. Alfred Russel Wallace's leading characteristics were devotion to truth and the perfect sincerity which follows from it, and his biographer shows a thorough understanding and a deep appreciation of his truly great character. The two volumes contain selections from thousands of letters written by and to Wallace, the most interesting undoubtedly being those which passed between him and Darwin during the years 1857—1881. These are given in full with no excisions and only some added notes of explanation. In the second volume accounts are given of Wallace's works and correspondence on biology and geographical distribution, and chapters are included on his social and political views and on in his work in astronomy and spiritualism. Wallace's name will live as that of a truly great investigator in his own line and an acute and advanced if not a deep thinker upon many subjects which lay outside his own special province, and his admirers have many reasons for gratitude to his biographer, who had an enthusiastic regard for the greatness of his personality and a profound admiration of his scientific attainments.

The Chemists' Year-Book, 1916. Edited by F. W. Black, M.Sc.Tech. (Manch.), B.Sc. (Lond.), A.I.C. London and Manchester: Sherratt and Hughes. Pp. 990. Price 10s. 6d. net. 1916.

This is a very useful handbook, which will be found a valuable addition to the libraries of the chemist and of technical colleges and schools. It contains a large amount of information, well arranged, well selected, and well indexed, and its appearance annually will confer a real benefit upon scientific men. Among the contents of the first volume may be noted a complete account of methods of inorganic qualitative and quantitative analysis and the ultimate analysis of organic substances, tables of the general properties of inorganic and organic compounds, and a good collection of mathematical tables, including five-figure logarithms and many useful conversion tables. The second volume contains tables of the physical constants of a very great number of substances and solutions, and also full accounts of the analysis of many technical products, including water, fuels, foods, alcoholic liquids, paper, textiles, dyes, and drugs.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Secretary announced the decease of the Right Hon. Sir James Stirling, P.C., LL.D., F.R.S., and Prof. Silvanus P. Thompson, D.Sc., F.R.S., Members of the Royal Institution, and resolutions of condolence with the relatives were passed. Mrs. Charles Chenevix Trench and Mr. James Watt were elected Members.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 19, May 8, 1916.

Catalysis of Hydrogen Peroxide in a Heterogeneous Medium. Third Part: Experiments with Oxides.—Georges Lemoine.—The results of the catalysis of hydrogen peroxide by ferric oxide differ very much according to the physical state and especially the state of division of the oxide. The author has studied the reaction in presence of the oxides of aluminium, cerium, silicon, and thorium, and gives the results of determinaminations of the rates of reaction. He discusses the possibility of the formation of peroxides with the insoluble oxides and comes to the conclusion that if they are formed they are very unstable.

Estimation of Carbon by the Eggertz Method.—H. Le Chatelier and F. F. Bogitch.—In the Eggertz colorimetric method of estimating carbon in steel the metal is usually dissolved in nitric acid of density 1·20 and kept for two hours at 80°, when the carbonaceous matter completely disappears. On cooling the coloration is compared with that of a standard liquid. The authors have modified the method by working always at the temperature of the boiling-point, and have studied separately the effects of varying the following factors—concentration of acid, speed of attack, exposure to light influence of the temperature of comparison, clearness of the coloured liquids, duration of heating, volume of the acid liquid, concentration of the acid, and purity of the acid. They have found that acids of density 1·18 to 1·15 effect the solution of the metal most rapidly, while those of density between 1·30 and 1·25 dissolve the carbonaceous matter quickest. Boiling should last for about five minutes, and it is best to use dilute acid to dissolve the metal and then add concentrated acid to effect the solution of the carbon.

MISCELLANEOUS.

Rubber from Alcohol.—L. I. Ostromislenskij describes in the *Petrograd Agricultural Gazette* a process patented by him for the preparation of rubber from alcohol. The process comprises two stages. Air is first pumped through the alcohol, and the mixed vapours are passed through copper tubes containing spirals of red copper and silver gauze. The latter are at first heated, but during the subsequent process remain incandescent. Acetic aldehyde and paraldehyde are thus formed. These are now mixed with more alcohol and passed over strongly heated aluminium oxide, producing erythrene, which is collected in an autoclave wherein a small quantity of a catalyst has been placed. Raw erythrene rubber, a pure chemical compound of formula $(C_4H_6)n$, is thus obtained, identical with chemically pure natural rubber but oxidising more rapidly, so that it is necessary to protect it from atmospheric action and fit it for use in other respects by adding about 15 per cent of admixtures. These are tannins to resist oxidation, amines mixed with lead oxide to aid in vulcanisation, and rubber resins to increase elasticity. This method of synthetic rubber production has been subjected to qualitative and quantitative tests by the Russian Government.—*South African Journal of Science*, xii., No. 8.

Literary Announcement.—The Ministry of Commerce, about which so much is now heard, is set out in full detail in a book which Messrs. Jarrold & Sons announce to appear immediately. The officials of the proposed Ministry, their salaries and their functions are minutely described, and the agitation for this new recognition of commerce is given a more definite shape. The author is Mr. Ernest J. P. Benn, a well-known trade journalist, who should be able to speak with knowledge on these matters, and his scheme for a complete system of trade associations headed by a Minister of Commerce is sure to provoke great interest in trading circles. The title chosen is "Trade as a Science," and the publishers promise that the work will be of intense interest to every trader great or small. Discussions on trading matters have a way of getting into the air and above the head of the average business man, and Mr. Benn is apparently going to try to bring them back to earth and within scope of each individual engaged in commerce. A preface is contributed by Lord Burnham, who comes to the conclusion that Mr. Benn's main premises are incontestible, and though the prosperity of Great Britain is based upon trade, there are few commercial countries where the dignity of trade has been held in less esteem, and few where trade has been less scientifically organised.

Society of Chemical Industry.—The Annual General Meeting will be held in Edinburgh on July 19, 20, and 21 next. The meeting, which will take the form of a Congress on the Progress of Chemical Industry in Great Britain since the outbreak of war, will be held in the Hall of the University Union, Teviot Place. Arrangements are being made for an exhibition on a moderate scale of British-made (1) dyes, (2) glass, and (3) porcelain to be on view during the meeting. It is hoped that this may add to the interest and value of the meeting. Members of the Society attending the Congress will be made members *pro tem.* of the Union, and will have all the rights and privileges of membership, including use of the reading, smoking, billiard, and dining rooms, and they may have letters addressed to them at the Union. Tickets of temporary membership of the Union will be issued at the office on or after July 18 to members of the Society on presentation of their tickets of membership. The office of the Society during the annual meeting will be at the University Union. As at last annual meeting, on account of present war conditions only those ladies who are members of the Society are invited to be present. Members who propose attending the meeting are requested to communicate at once with Dr. J. P. Longstaff, Chemistry Department, University of Edinburgh.

The following papers will be read:—

Prof. W. A. Bone, F.R.S., "Fuel."
Dr. G. P. Lishman, "Some Recent Improvements in Coke Works Practice."
Prof. H. Louis, "Waste in Coal Production."
D. R. Steuart, "The Shale Oil Industry."
W. H. Coleman, "A Short Review of the Influence exerted by the War on the Tar Distilling Industry."
G. T. Purves, "Extraction of Tar Fog from Hot Gas."
C. M. Whittaker (British Dyes, Ltd.), "Difficulties of Coal Tar Colour-making in War time."
D. B. Dott, "Production of Alkaloids as affected by the War."
F. H. Carr, "Manufacture of Synthetic Organic Drugs as affected by the War."
C. A. Hill and T. D. Morson, "Manufacture of Fine Chemicals in relation to British Chemical Industry."
J. F. Briggs, "The Paper Mill Chemist in War time."
J. W. Gordon, K.C., "Overhauling of our Patent Law."
W. F. Reid, "Influence of the Patent Laws upon Industry" (probable paper).
Bertram Blount, "Production of Glass for Scientific Purposes."
Dr. J. W. Mellor and B. Moore, "Pottery and Porcelain."
S. J. Johnstone, "Progress of British Rare Earth Industry during the War."

Erratum.—We regret that Figs. 1 and 4 in our last issue (p. 301 appear upside down. In the process of printing they were removed and re-inserted incorrectly.

THE CHEMICAL NEWS

Vol. CXIV., No. 2955.

THE SEPARATION OF THORIUM FROM IRON WITH THE AID OF THE AMMONIUM SALT OF NITROSOPHENYLHYDROXYLAMINE ("CUPFERRON").

By WILLIAM M. THORNTON, Jun.

The ammonium salt of nitrosophenylhydroxylamine, which was first introduced into analytical chemistry by O. Baudisch (*Chem. Zeit.*, 1909, xxxiii., 1298; 1911, xxxv., 913; Baudisch and King, *Journ. Ind. Eng. Chem.*, 1911, iii., 629), has been made a subject of study by several chemists (Nissenson, *Zeit. Angew. Chem.*, 1910, xxiii., 969; *Chem. Zeit.*, 1910, xxxiv., 539; Biltz and Hödtke, *Zeit. Anorg. Chem.*, 1910, lxvi., 426; Hanus and Soukup, *Ibid.*, 1910, lxviii., 52; R. Fresenius, *Zeit. Anal. Chem.*, 1911, l., 35; Bellucci and Grassi, *Gazz. Chim. Ital.*, 1913, xliii., 1, 570; Rodeja, *Anal. Fis. Quim.*, 1914, xii., 305; 1914, xii., 379; Ferrari, *Annali Chim. Appl.*, 1914, ii., 276; 1915, iv., 341; Turner, *Am. Journ. Sci.*, 1916, xli., 339). Because of its selective action as a precipitant many clean-cut separations have been effected, thus solving a variety of analytical problems which without the use of the reagent would involve much difficulty. Bellucci and Grassi (*loc. cit.*) have shown that in solutions decidedly acid with either sulphuric or hydrochloric acid the substance precipitates quantitatively titanium, and that under like conditions titanium can be completely separated from aluminium in one precipitation. Following the work of Bellucci and Grassi the author (*Am. Journ. Sci.*, 1914, xxxvii., 173; *Ibid.*, 1914, xxxvii., 407) has demonstrated that after throwing down the iron as ferrous sulphide from a solution containing sufficient ammonium tartrate to hold up titanium, and after acidifying the iron-free filtrate, the titanium can be quantitatively precipitated by the "cupferron" reagent notwithstanding the presence of tartaric acid, and further, that if the above-mentioned filtrate be strongly acidified with sulphuric acid and contain also a sufficient quantity of tartaric acid titanium can be quantitatively separated from both aluminium and phosphoric acid in one operation. Pursuing a similar technique E. M. Hayden, jun., and the author (*Am. Journ. Sci.*, 1914, xxxviii., 137) succeeded in separating zirconium from both iron and aluminium. During the same year Ferrari (*loc. cit.*) by means of the "cupferron" reagent separated zirconium from aluminium, but did not consider the more complicated case of iron being present as a third ingredient. Owing to the fact that thorium bears a marked resemblance to zirconium in its chemical relations, the author has seen fit to study the former element with respect to the "cupferron" reagent. The outcome of this investigation has been to establish conditions under which thorium is quantitatively precipitated by the reagent, and also to accomplish the indirect separation of thorium from iron.

A standard solution of thorium sulphate was employed for these experiments. This was prepared by dissolving the Welsbach Light Company's thorium nitrate in boiling water and precipitating the thorium with a boiling solution of sebacic acid according to the method of Smith and James (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 281). The thoroughly washed precipitate was dried and ignited to thorium oxide in a platinum dish. The residue was then subjected to a prolonged digestion with hot sulphuric acid. After cooling, the semi-solid mass was poured into cold water and the solution filtered from an insoluble residue of unattacked thorium oxide. The filtrate was made nearly neutral with redistilled ammonium hydroxide and the thorium precipitated with recrystallised oxalic acid. The thorium oxalate after complete washing was dried at 110° C. and the sample preserved. Of the oxalate thus obtained 8·5 grms. were digested with 50 cc. of sulphuric acid (made by diluting acid of sp. gr. = 1·84 with an equal volume of water), adding a little nitric acid to oxidise traces of organic matter which discoloured the liquid, and warming until nitric acid could no longer be detected by its odour. On pouring the residue into cold water the thorium sulphate dissolved completely and the solution was made up to a volume of one litre. Two experiments were made in order to set the standard of this solution. Weighed portions were treated with redistilled ammonium hydroxide at the boiling temperature, the resulting thorium hydroxide ignited to the oxide, and the latter brought to constant weight over the blast lamp. Duplicate determinations gave the following results:—

	Thorium sulphate solution.		Thorium oxide.	
(*a*)	25 cc.	25·740 grms.	0·0922 grm.	0·3582 per cent
(*b*)	25 cc.	25·757 "	0·0925 "	0·3592 "

The mean of these two values was taken as correct.

Preliminary experiments soon revealed the fact that even with very small concentrations of free sulphuric acid the precipitation of thorium by the "cupferron" reagent is incomplete. The author therefore resorted to the expedient of throwing out the thorium from a medium containing acetic as the only free acid. Accordingly weighed portions of 25 cc. of the standard thorium sulphate solution, containing also about 1·25 cc. of sulphuric acid (1 : 1), were taken and treated with 15 grms. of ammonium acetate in the form of a strong solution and the volume made up with water to 500 cc. A 5 per cent "cupferron" solution was then added gradually with constant stirring till present in some excess, 15 cc. being the volume actually used. The precipitate, after having been thoroughly coagulated by stirring, was thrown on to a paper filter and washed with a 1 per cent solution of ammonium acetate. The moist paper with its contents was then placed in a tared platinum crucible, dried at 100—110° C., and ignited first with the Bunsen burner and then with the blast lamp to constant weight. In this way the results of Table I. were obtained, which are within the limit of error for ordinary analytical work.

Table I.—*The Estimation of Thorium by Means of the "Cupferron" Reagent.*

No.	ThO_2 taken. Grm.	ThO_2 found. Grm.	Error. Grm.	$C_2H_3O_2NH_4$. Grm.	Volume of solution. Cc.
1.	0·0925	0·0924	−0·0001	15	500
2.	0·0923	0·0917	−0·0006	15	500

The thorium salt of nitrosophenylhydroxylamine—$[C_6H_5(NO).N.O]_4Th$, assuming a formula analogous to the one proposed by Bellucci and Grassi for the titanic derivative—differs a good deal in properties from the corresponding compound of either titanium or zirconium. In the case of the last two elements a high concentration of free sulphuric acid is consistent with total precipitation, while in the case of thorium extremely small concentrations of the same acid exert a marked solvent effect on the precipitate. Although very similar in appearance to the zirconium precipitate the thorium precipitate is rather different in texture; whereas the former permits filtration by suction the latter passes through the paper in small quantities under the influence of very light pressure. This is unfortunate from a manipulative standpoint, since the precipitate cannot be drained at the pump, necessitating the removal of included water by slow drying.

In the second series of experiments thorium was separated from iron. Known quantities of iron were taken by weighing off portions of pure dry ferrous ammonium sulphate. The solution (about 150 cc.), containing sufficient tartaric acid to hold up the bases in ammoniacal solution, was made slightly alkaline with ammonium hydroxide and colourless ammonium sulphide was added in moderate excess. After settling, the ferrous sulphide was filtered off and washed ten times with water containing a little colourless ammonium sulphide. Five cc. of sulphuric acid (1 : 1) were then added and the hydrogen sulphide thus liberated removed by boiling. After cooling to room temperature 25 grms. of ammonium acetate were added, the volume made up to 400 or 500 cc., and a 5 per cent "cupferron" solution added in decided excess. From this point on the determination was made just as in the case of thorium alone. Table II. contains the results of three experiments :—

Table II.—*The Separation of Thorium from Iron.*

No.	ThO_2 taken. Grm.	Fe_2O_3 taken. Grm.	ThO_2 found. Grm.	Error. Grm.	$C_2H_3O_2NH_4$. Grms.	Volume of solution. Cc.
3.	0·0924	0·1018	0·0922	−0·0002	25	400
4.	0·0924	0·1018	0·0916	−0·0008	25	500
5.	0·1846	0·1018	0·1840	−0·0006	25	400

A separation of thorium from iron with the aid of the "cupferron" reagent has been satisfactorily worked out and the experimental data show a fair degree of accuracy. Let the reader distinctly understand, however, that the above process is not offered as an analytical method for practical purposes. The well-known oxalate (see E. Benz, *Zeit. Angew. Chem.*, 1902, xv., 297) precipitation is satisfactory and separates thorium from nearly all the common elements with which it is likely to be associated. But another link has been added to the chain of "cupferron" results, and some comparative data on titanium, zirconium, and thorium with respect to this remarkable reagent have been brought to light which it is hoped will prove of interest.

Finally the author wishes to state that the experimental part of the work on thorium was carried out in the laboratory of the College of the City of New York, and to thank Prof. Charles Baskerville for fostering the investigation.

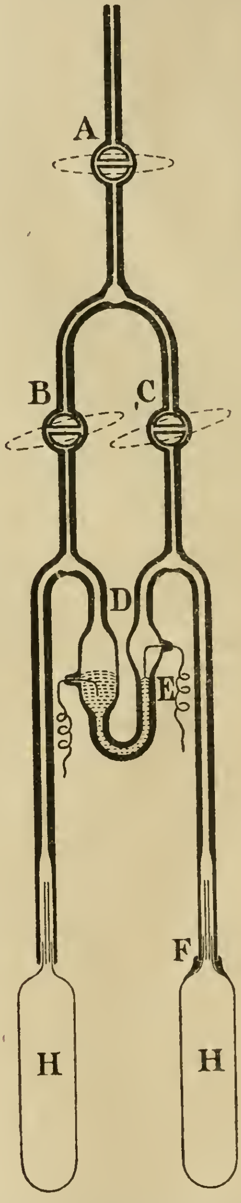
Wilmington, Delaware, June 6, 1916.

A SYNTHERMAL REGULATOR, A DEVICE FOR AUTOMATICALLY MAINTAINING AN ADIABATIC CONDITION IN CALORIMETRY.

By THEODORE W. RICHARDS and GEORGE D. OSGOOD

The method of adiabatic calorimetry, as recently developed in the Harvard Chemical Laboratories, demands that the bath surrounding the calorimeter should be changed in temperature at the same rate as the calorimeter itself, so that no heat should be lost or gained during the calorimetric determination. The outside bath has therefore been heated or cooled either by a suitable chemical reaction, or by hot or cold water, or by electricity (Richards, *Journ. Am. Chem. Soc.*, 1909, xxxi., 1280; see also Benedict and Higgins, *Ibid.*, 1910, xxxii., 462), so as to keep pace with the inside. Heretofore this quantitative identity of temperature has usually been established from moment to moment by the experimenter, who has observed both temperatures and acted accordingly. That this technique is feasible and accurate has been abundantly proved, but nevertheless with quick reactions the method makes considerable demands upon the operator; accordingly it seemed worth while to arrange an automatic device for relieving him of strain. Such a device might be called a "synthermal regulator."

Obvious methods for accomplishing this end will occur to any one familiar with this kind of problem. A multiple theremocouple or a pair of resistance thermometers might be connected with a delicate galvanometer in such a fashion that any inequality in the temperature of the two baths would cause a deflection in a galvanometer, and thus through a relay operate a mechanism for equalising the temperature, but it would be difficult to provide an adequate relay. A differential mercury-, or, better, a differential gas-thermometer might be used to attain the object sought, and this seemed much more promising. Because the relay seemed to be the crucial part of the contrivance, and because the last-named method requires a less sensitive relay than the others, it was tested first, and is described herewith. With a differential gas thermometer, in which contact is made between a very fine platinum point and a small meniscus, a fairly strong electric current may be sharply made and broken, and this, through a common long-distance tele-



Synthermal Regulator (about one-third actual size).

A, B, C, Glass stopcocks for filling and regulation; D, U-tube with bulbs containing mercury; E, very finely pointed platinum wire sealed in to make mercury contact; F, cement joint attaching H H, metal bulbs.

graph relay, can govern a powerful current capable either of directly heating the outside bath or of operating any desired mechanism for this purpose.

The differential thermometer took the form illustrated in Fig. 1. Two rounded copper or silver cylinders, holding each about 28 cc., were attached by de Khotinsky cement or sealing-wax (afterwards covered with paraffin to protect from caustic liquids) to a very narrow glass U tube (1·5 mm. diameter), with bulbs of familiar form. Suitable stopcocks were provided above, so that the whole contrivance could be filled with hydrogen (chosen because of its great conductivity) and conveniently adjusted. A finely pointed platinum wire, containing 8 per cent of iridium, was sealed into one of the bulbs, so as to make contact with mercury at the widening of the capillary U-tube. This differential thermometer is highly sensitive, quickly making and breaking contact within 1/100°. It should be set up with the platinum wire outward, so as to *make* the current when the inner vessel is the warmer. The electromotive force of the current employed should be moderately low, to diminish sparking, and the hydrogen must be pure to avoid combustion, because the removal of hydrogen in this way may cause changes in the setting. The current thus made and broken is sent through a good relay as already indicated.

With a regulating current thus made and broken it is possible, as stated, to operate a variety of mechanisms for regulating the temperature of the outer bath of the calorimeter. In our first experiments we used the strong current for turning on and off the flow of sulphuric acid into the outer bath, which contained alkali. The current was led through an electro-magnet, which operated a plunger-valve in the delivering vessel. For cooling reactions ice-water could obviously be delivered in a similar way. Unless the size of the jet is rather carefully proportioned to its task this device was found at times to admit too much liquid at once, overstepping the mark. We overcame this difficulty with a constant jet by cutting off the current every few seconds with the help of a constantly rotating circular key.

With apparatus thus constituted it was found that equality in temperature between the inside and outside vessels could be usually maintained within 0·02°, or at most 0·03°, even when the rise in temperature in the baths was rapid. With slow temperature changes the adjustment is even better. Thus it is capable of rendering real service in adiabatic calorimetry, and might also be useful in regulating a bath around apparatus for determining freezing points, or in other similar exigencies.

This apparatus was devised in the autumn of 1912. More recently one of us, with the collaboration of Dr. S. Tamaru, has used it in a different way; the stronger current of electricity from the relay was employed directly for heating the outside bath. Although not so suitable for very rapid reactions as the method of adding sulphuric acid to alkali, this method is very convenient for moderately slow ones, and we found that the regulator worked sufficiently well for many purposes when used in this way. In the course of this later work the importance of equality of pressure in the two metal bulbs at the moment of electrical contact became evident. This is easily adjusted by the stopcocks and slight tilting of the apparatus. Otherwise, of course, the quantity $\Delta p/\Delta t$ may be perceptibly different on the two sides, and therefore a progressing deviation of the two temperatures may occur.

The chief difficulty with very rapid reactions seems to be the lack of equable distribution of the heat, especially in the inner calorimeter vessel. If the different parts of this vessel are unequal in temperature of course the action of the differential thermometer will be irregular. Evidently very efficient stirring is necessary in both the inner and the outer vessel.

We are indebted to the Carnegie Institution of Washington for much of the apparatus used in these experiments.

Summary.

In brief, a delicate differential hydrogen thermometer with a sensitive mercury contact was devised. This, with the help of a relay, enabled a stronger current to operate a heating or cooling mechanism for causing one bath to follow the temperature of another within 0·03°. The apparatus, which may be called a "synthermal regulator," is of service in adiabatic calorimetry, or in other cases where identical but changing temperatures are desired in two contiguous vessels. — *Journal of the American Chemical Society*, xxxvii., No. 7.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.

By
GREGORY PAUL BAXTER, WILLIAM HENRY WHITCOMB, OLUS JESSE STEWART, and HAROLD CANNING CHAPIN.

In an earlier investigation on the atomic weight of neodymium by Baxter and Chapin (*Proc. Amer. Acad.*, 1911, xlvi., 213; *Journ. Am. Chem. Soc.*, xxxiii., 1; *Zeit. Anorg. Chem.*, lxx., 1) the material examined was purified first by crystallisation of the double ammonium nitrate and then by crystallisation of the nitrate from concentrated nitric acid. The first process was found particularly successful in eliminating samarium, the second in freeing the neodymium from praseodymium. The fractions in the final series were converted to chloride, which after very careful dehydration was analysed by comparison with silver, with the result that the atomic weight of neodymium was found to be 144·27 (Ag = 107·880).

During the purification of the neodymium material as described above attempts were made to free the neodymium from its companions by other methods. One of these was the fractional crystallisation of the chloride. This crystallisation proceeds less readily than that of either the double nitrate or nitrate, and after the process had been carried on for ten series of crystallisations little evidence of separation could be observed. At the same time another portion of the original material was converted to nitrate and fractionally crystallised from concentrated nitric acid. As the chief impurity, praseodymium, seemed to accumulate rapidly in the more soluble fractions, the portion which had been crystallised as chloride also was converted to nitrate and fractionally crystallised from nitric acid. Fractional crystallisation of these two portions was carried on separately for some time, for seventy-five series with one portion, for seventy-six with the other; then the two portions were combined and further crystallised in the same way. Both the least soluble and the most soluble fractions frequently were rejected, the least soluble fraction to eliminate samarium, gadolinium, &c., the most soluble to remove praseodymium, cerium, and lanthanum, for Demarçay has shown that the separation occurs in this order (*Comptes Rendus*, 1896, cxxii., 728; 1900, cxxx., 1021). The least soluble fraction was thus forty times discarded, the most soluble eighty-four times. After 158 series of crystallisations in all had been carried out the purity of the fractions of the last series, seventeen in number, was investigated spectroscopically. As all of the fractions seemed to be fairly pure and the intermediate fractions very pure, it was decided, for the purpose of comparison with the material purified for the earlier investigation, to examine quantitatively the new material. Since at the outset only one and one-half kilogrms. of fairly pure double ammonium nitrate was used the final fractions were not large, and therefore instead of analysing each fraction separately they were combined in pairs, except that the three least soluble fractions—2590, 2591, and 2592—were combined. The combinations actually analysed were:—2590 + 2591 + 2592, 2593 + 2594, 2595 + 2596, 2597 + 2598, 2599 + 2600, 2601 + 2602; 2603 + 2604.

The purity of each of these combinations was carefully determined by photography of the visible and ultraviolet regions of the absorption spectrum with a Féry quartz spectrograph. The solutions were prepared by dissolving 2 grm. portions of the ignited oxides in a slight excess of nitric acid and diluting the solution to a volume of about 10 cc. The absorbing layer was 10 cm. long. The less soluble fractions contained small amounts of samarium and the more soluble ones praseodymium. In order to determine the proportions of these impurities, to a solution of a 2 grm. portion of the oxide of Fraction 2605—6, which was free from samarium although it contained praseodymium, were added known amounts of a standard solution of pure samarium nitrate, the absorption spectrum of the solution being photographed after each addition of samarium. (The samarium material was very kindly furnished by Prof. C. James, of New Hampshire College). By comparing photographs of the different fractions with those of the material containing known amounts of samarium, it was possible to estimate with considerable exactness the proportion of samarium (through the band λ 401) in the former. The percentage of praseodymium (through the band λ 444) in the more soluble fractions was estimated in a similar fashion by comparing the photographs of the fractions analysed with those of a solution of Fraction 2590—1—2, to which known amounts of praseodymium were added. The results of these comparisons are given below:—

Fraction.	Samarium. Per cent.	Fraction.	Praseodymium. Per cent.
2590—2591—2592	0·6	2599—2600	0·00
2593—2594	0·4	2601—2602	0·05
2595—2596	0·2	2603—2604	0·1
2597—2598	0·1	2605 – 2606	0·2
2599—2600	0·0		

Since cerium and lanthanum nitrates are both more soluble in concentrated nitric acid than praseodymium nitrate the quantities of thess impurities remaining must have been very small indeed.

Although the proportions of impurity are small, yet because the atomic weights of both samarium and praseodymium are considerably different from that of neodymium it is not surprising that the extreme crystal fraction yielded a result somewhat higher than the average and that the more soluble fractions apparently possessed an atomic weight slightly lower than the average. However, since the amounts of impurity were determined with some accuracy corrections could be applied to the final result.

Preparation of Materials.

The Preparation of Neodymium Chloride.—In order to change the nitrate to chloride essentially the same processes were employed as in the previous investigation. Neodymium oxalate was first precipitated by adding to the dilute solution of the nitrate a considerable excess of oxalic acid. The oxalate was collected upon a disc of filter-paper in a porcelain Gooch crucible, and after being dried was ignited to oxide in a platinum boat in an electrically heated porcelain tube, pains being taken to avoid heating the boat to a temperature at which platinum might vaporise into the contents (see Baxter and Chapin, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 16). The resulting oxide was dissolved in redistilled nitric acid in a quartz dish and after the solution had been diluted the oxalate was reprecipitated by means of a dilute solution of either recrystallised oxalic acid or recrystallised ammonium oxalate. The oxalate was washed, dried, and ignited as before; then it was dissolved in a quartz dish in hydrochloric acid which had been distilled through a quartz condenser, and the chloride was at least three times crystallised in quartz dishes by saturating the aqueous solution with hydrochloric acid gas at a low temperature. Centrifugal drainage of the crystals was always employed. The product was preserved in quartz in a desiccator containing fused sodium hydroxide.

Reagents.—Pure silver, water, and reagents were prepared exactly as recently described in the account of similar work by Baxter and Stewart on praseodymium chloride (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 524).

The Drying of Neodymium Chloride.—In the earlier work by Baxter and Chapin the attempt was made to prepare the salt for analysis by drying it carefully in a current of hydrochloric acid gas and eventually fusing the salt. In the first experiments the salt dried in this way invariably yielded a considerable amount of insoluble material, the exact nature of which was not discovered until later. Hence the expedient was adopted of drying the salt for analysis as carefully as possible below the fusing temperature and then determining the proportion of water retained. Ultimately it was found possible to obtain fused salt which would yield a perfectly clear solution, but the necessary information as to the proper treatment was obtained too late to be of service. It was partly because of the slight uncertainty involved in applying a correction for the residual water that the present investigation was undertaken. In the recent research by Baxter and Stewart upon praseodymium chloride a similar difficulty was met (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 527), and in the latter research it was shown that the insoluble material is the oxychloride, and that its formation can be wholly or almost completely avoided by drying the salt as completely as possible previous to fusion and then fusing the salt as rapidly as possible. No matter how carefully the preliminary drying is carried out, and no matter what precautions are taken in the drying of the hydrochloric acid gas in which the salt is fused, prolonged fusion invariably yields a very considerable proportion of insoluble matter, probably owing to a small amount of air contained in the hydrochloric acid gas. In these respects the neodymium chloride resembles the praseodymium salt exactly. A considerable amount of the insoluble neodymium compound was prepared by fusing some of the carefully dried chloride for an hour. The insoluble residue was collected and weighed and its content of neodymium and chloride was determined. The results of these experiments indicate conclusively that the insoluble matter is the oxychloride. The following table contains the results of these experiments:—

Weight of insoluble material	0·00775	grm.
„ AgCl found	0·00602	„
„ AgCl calculated from NdOCl	0·00568	„
„ Nd_2O_3 found	0·00685	„
„ Nd_2O_3 calculated from NdOCl	0·00666	„

By following the same procedure in the drying of the neodymium chloride that was used in the drying of the praseodymium chloride we were able to prepare salt which yielded immediately a clear solution. The details of this procedure are as follows:—A platinum boat containing the powdered crystals of the hydrated salt was placed in a quartz tube forming part of a Richards "bottling apparatus." The bottling apparatus, which contained the weighing bottle in which the boat had initially been weighed, was connected with an apparatus for delivering dry hydrochloric acid gas, nitrogen, and air. This apparatus is described in the paper on praseodymium chloride (*Ibid.*, 1915, xxxvii., 526). The boat was then gradually heated to a temperature slightly above 100° but considerably lower than the transition temperature of the salt, 124°, until nearly all of the first five molecules of water of crystallisation had been expelled by efflorescence. The temperature was then raised to 180° or thereabouts, where the sixth molecule of water evaporates, and finally the salt was heated to about 350° for several hours. The aluminium block oven which had been used for producing uniform temperature up to this point was now replaced by an electrically heated sleeve, and the salt was brought to the fusing-point, 785°, as quickly as possible (Matignon, *Comptes Rendus*, 1901, cxxxiii., 289; 1905, cxl., 1340). Then it was allowed to cool rapidly, and after the acid gas had been displaced by nitrogen and finally by air the boat

TABLE I.—*The Atomic Weight of Neodymium.*

$NdCl_3 : 3Ag$.

Ag = 107·880. Cl = 35·457.

Number of analysis.	Analyst.	Fraction.	Weight of $NdCl_2$ in vacuum. Grms.	Weight of Ag in vacuum. Grms.	Weight of Ag added or subtracted. Grm.	Corrected weight of Ag in vacuum. Grms.	Ratio $NdCl_3 : 3Ag$.	Atomic weight of Nd.
1	Whitcomb..	2590—1—2	3·34038	4·31322	−0·00035	4·31287	0·774514	144·293
2	Stewart ..	2590—1—2	4·03869	5·21540	−0·00095	5·21445	0·774519	144·294
						Average ..	0·774517	144·294
3	Whitcomb..	2593—4	4·48251	5·78795	−0·00035	5·78760	0·774503	144·289
4 (*a*)	Whitcomb..	2593—4	3·75204	4·84483	−0·00025	4·84458	0·774482	144·282
5	Stewart ..	2593—4	6·00909	7·75942	−0·00050	7·75892	0·774475	144·280
						Average ..	0·774487	155·284
6	Whitcomb..	2595—6	4·96466	6·41065	−0·00020	6·41045	0·774464	144·276
7 (*a*)	Whitcomb..	2595—6	4·15431	5·36422	−0·00030	5·36392	0·774492	144·285
8	Stewart ..	2595—6	5·53210	7·14341	−0·00003	7·14338	0·774437	144·268
						Average ..	0·774464	144·276
9 (*a*)	Whitcomb..	2597—8	4·73995	6·12054	0·00000	6·12054	0·774433	144·267
10	Whitcomb..	2597—8	4·22430	5·45464	−0·00020	5·45444	0·774470	144·278
11	Stewart ..	2597—8	5·93271	7·66037	+0·00051	7·66088	0·774416	145·261
						Average ..	0·774440	144·269
12	Whitcomb..	2599—2600	5·60324	7·23524	0·00000	7·23524	0·774439	144·268
13	Stewart ..	2599—2600	7·22817	9·33324	+0·00035	9·33359	0·774426	144·264
						Average ..	0·774433	144·266
14	Whitcomb..	2601—2	5·16230	6·66582	+0·00020	6·66603	0·774419	144·262
15	Stewart ..	2601—2	4·50348	5·81508	+0·00050	5·81558	0·774382	144·250
						Average ..	0·774401	144·256
16	Whitcomb..	2603—4	6·42333	8·29438	0·00000	8·29438	0·774419	144·262
17	Stewart ..	2603—4	7·59534	9·80745	+0·00077	9·80822	0·774385	144·251
						Average ..	0·774402	144·256

TABLE II.—*The Atomic Weight of Neodymium.*

$NdCl_3 : 3AgCl$.

Ag = 107·880.

Number of analysis.	Analyst.	Fraction.	Weight of $NdCl_3$ in vacuum. Grms.	Weight of AgCl in vacuum. Grms.	Loss on fusion. Grm.	Total dissolved AgCl. Grm.	Corrected weight of AgCl. in vacuum. Grms.	Ratio $NdCl_3 : 3AgCl$.	Atomic weight of Nd.
18	Stewart ..	2590—1—2	4·03869	6·92658	0·00048	0·00176	6·92786	0·582963	144·310
19	Whitcomb..	2593—4	4·48251	7·68865	0·00016	0·00156	7·69005	0·582897	144·281
20 (*a*)	Whitcomb..	2593—4	3·75204	6·43617	0·00041	0·00162	6·43738	0·582852	144·262
21	Stewart ..	2593—4	6·00909	10·30826	0·00056	0·00106	10·30876	0·582911	144·287
							Average ..	0·582887	144·277
22	Whitcomb..	2595—6	4·96466	8·51602	0·00033	0·00065	8·51634	0·582957	144·307
23 (*a*)	Whitcomb..	2595—6	4·15431	7·12648	0·00056	0·00151	7·12743	0·582862	144·266
24	Stewart ..	2595—6	5·53210	9·49047	0·00031	0·00118	9·49134	0·582858	144·264
							Average ..	0·582892	144·279
25 (*a*)	Whitcomb..	2597—8	4·73995	8·13139	0·00014	0·00107	8·13232	0·582853	144·262
26	Whitcomb..	2597—8	4·22430	7·24613	0·00018	0·00119	7·24714	0·582892	144·279
27	Stewart ..	2597—8	5·93271	10·17821	0·00025	0·00095	10·17891	0·582844	144·258
							Average ..	0·582863	144·266
28	Whitcomb..	2599—2600	5·60325	9·61209	0·00019	0·00109	9·61299	0·582883	144·275
29	Stewart ..	2599—2600	7·22817	12·40020	0·00024	0·00102	12·40098	9·582871	144·270
							Average ..	0·582877	144·273
30	Whitcomb..	2601—2	5·16230	8·86100	0·00090	0·00137	8·86147	0·582556	(144·134) (*b*)
31	Stewart ..	2601—2	4·50348	7·72660	0·00025	0·00083	7·72718	0·582810	144·244
32	Whitcomb..	2603—4	6·42333	11·02125	0·00078	0·00237	11·02284	0·582729	(144·209) (*b*)

(*a*) The neodymium chloride used in these experiments was heated almost but not quite to the fusing-point.

(*b*) The results of Analyses 30 and 32 are inexplicably low. As they were the first two experiments carried out by Mr. Whitcomb we feel that it is justifiable to omit them in the final treatment of the results.

and contents were transferred to the weighing bottle without exposure to moisture and weighed. In a few cases a trace of insoluble salt was visible when the chloride was dissolved in water, but the proportions in these cases, judging from earlier experience, were less than 0·1 mgrm. By allowing the solution to stand for a day or two the basic salt dissolved completely. In Analyses 1, 2, 3, 5, 11, 13, 15, 16, 17, 18, 19, 21, 27, 29, 31, and 32 the solution of the chloride was clear at the outset.

Since the basic salt seems to form through the action of the air in the hydrochloric acid upon the fused salt more readily at higher than at lower temperatures, in three experiments the salt, after the usual careful preliminary drying, was heated almost but not quite to the fusing-point for some time. In this way all but negligible amounts of water must have been expelled. In fact these analyses (Nos. 4, 7, 9, 20, 23, and 25) show a slightly greater percentage of chlorine rather than smaller than the specimens which were actually fused. In these cases also the salt yielded a perfectly clear solution.

The Method of Analysis.

The method of analysis was like that previously used with neodymium and praseodymium and other chlorides. The salt was dissolved in water and the solution was diluted to a volume of 1000—1500 cc. in a glass-stoppered precipitating flask. Pure metallic silver equivalent to the chloride within a very few tenths of a mgrm. was weighed out, dissolved in nitric acid, and diluted to about the same volume. (The silver used had already been tested in the praseodymium work). The silver solution was then added to the chloride solution in small portions with frequent agitation. After standing at room temperature for some time the analysis was cooled to 0·0° in order to reduce the solubility of silver chloride (Richards and Willard, *Journ. Am. Chem. Soc.*, 1910, xxxii., 32), and the clear solution was tested in a nephelometer for excess of chloride or silver. The estimated deficiency of either was added in the form of hundredth normal solution, and the solution was again thoroughly shaken, allowed to clarify and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used.

In the analyses by Mr. Whitcomb, after the end-point of the comparison had been reached an excess of 0·05 grm. of silver nitrate was added for each litre of solution, and the analyses were allowed to stand some time longer at 0·0°. Then the silver chloride was washed several times with ice-cold silver nitrate solution containing 0·05 grm. per litre and many times with ice-cold water before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically heated air-bath at 190° for at least eighteen hours and weighed. Residual moisture was determined by the loss in weight when the main bulk of the precipitate was fused in a porcelain crucible. The weight of silver chloride dissolved in one litre of the filtrate and silver nitrate washings was assumed to be 0·000004 grm. per litre (calculated from the solubility product of silver chloride at 0·0° as found by Kohlrausch, 9×10^{-12}—*Zeit. Phys. Chem.*, 1908, lxiv., 167). Chloride dissolved in the aqueous washings together with that obtained from the precipitating flask was estimated by nephelometric comparison with standards.

In the analyses by Mr. Stewart, after a similar excess of silver nitrate had been added, the system was allowed to stand at room temperature for several days before filtration. In computing the correction for silver chloride dissolved in the filtrate and silver nitrate washings, which were not chilled, the assumption is made that the solutions were saturated at 25°, since the experiments were carried out during the summer months. Using Kohlrausch's determination of the solubility product of silver chloride at 25°, $1·7 \times 10^{-10}$, the solubility in 0·0003 normal silver nitrate is 0·00008 grm. The aqueous washings were chilled to diminish the solubility of the precipitate and were analysed nephelometrically.

The main mass of silver chloride was dried at 158° and the moisture retained was found from the loss on fusion.

In Mr. Whitcomb's experiments the portions of the original solution removed for nephelometric comparisons were returned and a correction applied for the silver chloride thus introduced. In Mr. Stewart's experiments the test portions were rejected and a correction of 0·00005 grm. was added for each 100 cc. of solution removed.

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were standardised to hundredths of a mgrm. by the Richards substitution method (*Journ. Am. Chem. Soc.*, 1900, xxii., 144). The following vacuum corrections were applied :—

	Specific gravity.	Vacuum correction per grm.
Weights ..	8·3	
$NdCl_3$ ..	4·134	+0·000145
AgCl	5·56	+0·000071
Ag	10·49	−0·000031

TABLE III.

Fraction.	$NdCl_3$: 3Ag.	$NdCl_3$: 3AgCl.	Average of all analyses.	Corrected average of all analyses.
2590—1—2	144·294	144·310	144·299	144·263
2593—4	144·284	144·277	144·280	144·256
2595—6	144·276	144·279	144·278	144·266
2597—8	144·269	144·266	144·268	144·262
2599—2600	144·266	144·273	144·269	144·269
2601—2	144·256	144·244	144·252	144·254
2603—4	144·256	—	144·256	144·259
			Av.	144·261

The results with the different fractions are summarised in Table III.. in the last column of which corrections also are made for praseodymium and samarium impurity, on the basis of the atomic weights 140·9 and 150·4 respecttively.

TABLE IV.

Analyses.	Ag : AgCl.
2 and 18	0·752678
3 and 19	0·752609
4 and 20	0·752570
5 and 21	0·752653
5 and 22	0·752723
7 and 23	0·752574
8 and 24	0·752621
9 and 25	0·752619
10 and 26	0·752633
11 and 27	0·752623
12 and 28	0·752652
13 and 29	0·752649
14 and 30	(0·752249) (*a*)
15 and 31	0·752613
16 and 32	(0·752472) (*a*)
Av.	0·752632

(*a*) See Note *b*, p. 17.

The concordance of the results with each fraction is satisfactory. It is interesting to note that with the ununcorrected results a perceptible difference exists between the head and tail of the series, and that this difference largely disappears when corrections are applied for rare earth impurity. The uncorrected results with the purest fractions and the corrected result with all the fractions differ very little from Baxter and Chapin's earlier result, 144·275 (Ag = 107·880).

In Table IV. the ratio of silver used to silver chloride obtained in the same experiment is given for all complete pairs of analyses. Since the average ratio is essentially identical with that found by Richards and Wells (*Publ. Carnegie Inst.*, 1905, xxviii. ; *Journ. Am. Chem. Soc.*, 1908, xxviii., 456), 0·752634, it can reasonably be concluded that errors from occlusion by the silver chloride or from loss of silver chloride are absent. This is in accord with earlier experience of the same kind.

Summary.

Neodymium nitrate was purified by fractional crystallisation of the nitrate from concentrated nitric acid. Chloride, prepared from the final fractions of nitrate, was analysed by comparison with silver. The atomic weight of neodymium was thus found to be 144·261. The average of this result and that found earlier by Baxter and Chapin, 144·275, is 144·268. The rounded-off figure 144·27 (Ag = 107·88) seems to represent fairly the final outcome of both researches.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance, as well as to Dr. H. S. Miner, of the Welsbach Light Company, for the neodymium material.—*Journal of the American Chemical Society*, xxxviii., No. 2.

THE CONTENT, METHOD, AND RESULTS OF THE HIGH SCHOOL COURSE IN CHEMISTRY.*

By ALEXANDER SMITH, Columbia University, New York City

(Concluded from p. 8).

The Method.

In striving for the desired results, success depends entirely on the methods used. We have time for a single illustration only. In live chemistry, is it necessary to pay attention to physics? Many texts suggest an answer in the negative. In their introductions they labour to distinguish between chemistry and physics, and leave the impression that, when the distinction has been formulated, the physics will be identified wherever found, and will be eliminated. Let us analyse the situation in practical chemistry. How is chemical change brought about? Some people say by chemical means. One recent author says that mere mixing does not produce chemical change, as if mixing solutions did not produce chemical actions in hundreds of cases, and as if mixing suitable substances with chlorine was not almost always sufficient to start the reactions. Rubbing salt in a mortar is a physical operation, but tapping fulminating mercury and tickling iodide of nitrogen with a feather are apparently chemical means! Boiling water is physical, but boiling liquid nitrogen trioxide is chemical. Precipitation is due to physical immiscibility, and is physical. Heating increases the speed of motion of the molecules and is a physical, and, indeed, literally, a mechanical means of producing chemical change. Even electrolysis consists in shooting a stream of electrons at the solution, and is now mechanical. All the means we use are physical.

Again, heating a platinum wire is a physical phenomenon. When we decompose mercuric oxide by heating, what sort of a phenomenon is it? A phenomenon is something seen, or more generally something perceived by the senses. We collect the gas given off, and we see the mercury accumulating on the wall of the tube. Certainly, the *phenomena* are physical here, also. We even reason physically, for the mercury cannot come from nothing, so we conclude that it is condensing from an invisible vapour. During the process the mass of the oxide becomes less and less. All that we can perceive by the senses is physical.

A certain group of these physical phenomena is not only physical but also chemical. The sub-group is easily defined when the time comes. If one substance gives two or two give one, or two give two, all the substances concerned being different, then the phenomenon, in addition to being a physical is also a chemical change; or, if the composition of a material is such that the elements are present in proportions that can be represented by multiples of the atomic weights by whole numbers, then it is a chemical compound (*e.g.*, a hydrate); if the proportions are not of this nature (*e.g.*, a solution), then it is a physical aggregate.

Thus we use physical means to produce chemical change because they are the only means available. We study the resulting physical phenomena to learn what the change was because they are the only phenomena; we reason in physical terms about the phenomenon, in order to understand and to classify it, because physical data are the only data available; finally we draw the conclusion that it was a chemical change, altering certain substances into certain other substances.

Many teachers of chemistry do not realise how far physics dominates the experimental work in chemistry. On distributing standard texts to the members of a class made up largely of teachers of chemistry, and asking them to report as to certain specific features of the text assigned to each, I have frequently instructed them to consider whether the physics required in practical chemistry was adequately represented. The almost invariable report was, "Yes; Boyle's and Charles' laws are in the book!" Suppose we were rigidly to exclude all physics, including physical properties and phenomena, from the course in chemistry, what would happen? We could not describe common salt, because the solid state, whiteness, and cubical crystalline form would be lacking.

It is evident that a very specific and ready knowledge of many parts of physics will be acquired in connection with a course in live chemistry. The physics need not be called physics, nor need it be forced, for it comes in quite naturally. What physical property of oxygen enables us to utilise the oxygen we draw into our lungs? Evidently its solubility in the moisture on the inner surface of the lungs. When we burn phosphorus in oxygen the pentoxide form an immense cloud of particles and nothing remains in the spoon, but when we burn iron wire in oxygen no such smoke is formed and the oxide remains in globules. Why this difference? In classes of freshmen in college, all of whom have admission credit in chemistry, I have never received a sensible answer to this question. The question is asked of course to show them that even from experiments they have nearly all seen before there may still be something of an obvious nature that they had never considered. The few who venture a reply say that the pentoxide must be lighter than air, an explanation disproved by the fact that the substance in a bottle on the table is in the bottom of the bottle.

Is this real chemistry? The problems of the chemical industries seldom concern the chemical reaction itself. The difficulties almost all arise because of the physical properties of the crude materials and of the products. In the contact process for sulphuric acid the difficulty did not lie in the reaction, which had long been known, but in the poisoning of the catalyst by foreign substances transported mechanically by the gases. Again, a novice would expect the sulphur trioxide to dissolve easily in water, but it was found that the excess of oxygen used in the process carried a large part of the oxide right through the water and out of the absorbing units. Investigation showed that 97 to 98 per cent sulphuric acid absorbed it much more completely, and so the acid itself is employed for the purpose.

Is this good education? Well, it teaches closer observation whenever the real facts are wanted; it substitutes simple reason for memorising; it teaches the need of alertness and penalises superficiality; it calls attention to facts rather than words as the subject of study; it is not physical chemistry, which is a theoretical subject, but practical chemistry. It would seem, therefore, that we should give attention to the physical means used to produce chemical changes, that we should show how a hemical change must be explored by physical means and how it must be described in physical terms. Prof Cooley once said, "An experiment is a question put to nature, and forethought and care are required in putting the question and study and reflection in interpreting the answer." We may add to this that a chemical experiment is a question put by physical means and the reply comes in the form of physical phenomena. The physical language is the only one that practical chemistry can understand or speak. Physics is the language of live chemistry, and without attention to the physics chemistry is both deaf and dumb.

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* Address before the Science Section of the New York State Teachers' Association. From *School Science and Mathematics*, 1916, xvi.

Conclusion.

Live chemistry must utilise the arithmetic, English, physics, scientific method, and other previous acquisitions of the pupil. It must include vital connections with the chemistry of nature and of the industries. This will be real chemistry if the pupil continues the subject and real education if he does not. The method must emphasise facts and relations rather than words. As containing a new subject-matter, the course exercises the pupil in applying standard methods to new problems, with the possibility that he may learn later to use the same methods in business and in life, and so become a rational and successful citizen. The basis is in the book, but the connections and how to make them depend upon the laboratory work and the teacher. Live chemistry is the kind taught by a live teacher, and so after all the results depend entirely upon the knowledge, skill, and alertness of the teacher.

NEW METHODS FOR THE ANALYSIS OF LIME-SULPHUR SOLUTIONS.*

THE ESTIMATION OF "POLY-SULPHUR."

By ROBERT M. CHAPIN,
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WHATEVER may be the actual atomic grouping of sulphur in the various calcium polysulphides which constitute the important ingredient of lime-sulphur solutions it is convenient to discuss the combinations of the element as if it occurred therein in two distinct forms—namely, "mono-sulphur" and "poly-sulphur." The general formula for these calcium polysulphides may then be expressed as $Ca(m\text{-}S)\ (p\text{-}S)_y$. A previous paper (*Journ. Ind. Eng. Chem.*, 1916, viii., 151) on the analysis of lime-sulphur solutions has described among other things the estimation of mono-sulphur. In continuation of the work a volumetric method now has been developed for the estimation of poly-sulphur, with apparently a desirable degree of both accuracy and convenience.

Description of the Method.

That the reaction $S + Na_2SO_3 = Na_2S_2O_3$ applies to the poly-sulphur of soluble polysulphides has long been known. The reaction $Ca(m\text{-}S)\ (p\text{-}S)_y + yNa_2SO_3 = CaS + yNa_2S_2O_3$ is the basis of the new method. Mono-sulphur is removed as zinc sulphide and excess of sulphite as insoluble strontium sulphite, after which thiosulphate is determined by titration with iodine. From the total thiosulphate thus obtained must naturally be subtracted the thiosulphate originally present in the lime-sulphur solution. The detailed execution of the method is as follows:—

Into a mixture of 10 cc. of a recently prepared 10 per cent solution of C.P. anhydrous sodium sulphite and 20 cc. of N/5 ammoniacal zinc chloride, contained in a 200 cc. Erlenmeyer flask, pipette 10 cc. of a dilution of the sample containing 1·5 to 2 per cent "sulphide sulphur." Mix, wash down with about 25 cc. water and place on the steam-bath at full heat. At intervals of ten minutes mix the contents of the flask and rinse down with a little hot water from a wash-bottle. After heating for 45 minutes with four intermediate mixings remove from the heat, add 20 cc. of a 10 per cent solution of crystallised strontium chloride, and mix well. Let settle for five minutes, then filter into a 250 cc. volumetric flask and wash with hot water. Cool in water to room temperature, add 0·5 to 1·0 cc. of a 10 per cent solution of crystallised disodium phosphate, make to the mark, shake well and filter through a dry paper into a dry flask, first using about 20 cc. to wet the paper, the runnings being discarded. To 200 cc. of the clear filtrate add methyl red indicator, then slowly and with thorough mixing a 10 per cent solution of tartaric acid to a permanent slight acid reaction. Add starch and titrate with N/10 iodine. The whole process should be executed without intermediate delays. From the observed iodine titration subtract a blank of 0·10 cc., multiply the remainder by 1·25 to convert to the basis of 10 cc. lime-sulphur solution, and from this figure subtract the "thiosulphate figure" previously obtained (*Journ. Ind. Eng. Chem.*, 1916, viii., 151). The resultant figure is the "poly-sulphur figure" of the lime-sulphur solution as diluted for analysis—that is it represents cc. of N/10 iodine, equivalent to the poly-sulphur in 10 cc. of diluted lime-sulphur in the ratio of one atom of iodine to one of sulphur.

From the titration "figures" mentioned in this and the previous paper are naturally calculable the percentages of the various forms of sulphur existing in the diluted lime-sulphur solution, according to the following formulæ:—

Sulphide-acid figure $\times$ 0·0016035 $\times$ 10 = per cent mono sulphur.
Poly-sulphur figure $\times$ 0·003207 $\times$ 10 = per cent poly-sulphur.
Thiosulphate figure $\times$ 0·006414 $\times$ 10 = per cent thiosulphate sulphur.

Helpful Notes on the Execution of the Method.

1. The zinc solution is best prepared by dissolving about 6·537 grms. of C.P. metal in some excess of hydrochloric acid, diluting to about 900 cc., adding sufficient concentrated ammonia to obtain a clear solution, and then diluting to 1000 cc. The zinc solution is to be used in 50 to 100 per cent excess of the amount called for by the previously described "sulphide-acid figure," for the precipitated zinc hydroxide is relied upon to render filterable the finely divided strontium sulphite.

2. In order to be certain that sufficient sodium sulphite is present it is well to measure in slightly different amounts in duplicate determinations, in which case the duplicates cannot check if sufficient sulphite has not been added.

3. The volume of sodium phosphate solution is varied between 0·5 and 1·0 cc., depending on the amount of strontium sulphite which appears to have passed the first filter. Even if no precipitate is visible this step must not be omitted. The non-appearance of a considerable precipitate of strontium phosphate would of course indicate an insufficient addition of strontium chloride. In the final filtration from the strontium phosphate a plaited filter may be used with considerable saving of time if the filtrate is repassed until perfectly clear.

4. Tartaric acid is known to promote liberation and decomposition of thiosulphuric acid far less rapidly than do mineral acids in equivalent excess, and is therefore much preferable.

5. The necessity for subtraction of the blank from the observed iodine titration will be discussed in the experimental section of this paper.

6. Both mono-sulphur and poly-sulphur are calculated from titrations which must be corrected for the amount of thiosulphate originally present in the lime-sulphur solution. The accurate determination of thiosulphate therefore becomes a matter of much importance. In the experience of the writer methods which involve aliquot filtration from precipitated mono-sulphur and poly-sulphur are prone to

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yield somewhat low and irregular results, apparently owing to adsorption of thiosulphate by precipitated sulphur and sulphides (compare Thompson and Whittier, Delaware College Agricultural Experiment Station, *Bull.* 105, p. 7). The following method is therefore advised for the determination of thiosulphate:—Into 20 cc. of N/5 ammoniacal zinc chloride contained in a 150 cc. beaker pipette 10 cc. of the diluted lime-sulphur solution. Mix, dilute to about 75 cc., heat on the steam-bath 30 minutes with occasional stirring, then filter and wash with hot water. Cool the filtrate, add about 1 grm. C.P. potassium iodide, methyl red indicator, and cautiously render slightly acid with 10 per cent tartaric acid, finally titrating with iodine.

Experimental.

The scheme at first investigated was to pipette the sample into a freshly boiled and hot solution of sodium sulphite and ammonia, boil a sufficient length of time, and then to add both ammoniacal zinc chloride and strontium chloride, after which the determination was completed as in the regular method. This procedure is more rapid and by the speed of decolorisation indicates to the eye whether sufficient sulphite has been employed. Two obvious objections are that excess lime may react with some poly-sulphur, producing low results, and that some mono-sulphur may become oxidised, producing high results. With the object of testing these sources of error the regular method previously outlined was tried, without, it must be confessed, much hope that the sodium sulphite would successfully perform its function upon precipitated poly-sulphur. When such was found to be the case the first conceived method was abandoned, at least for the present, for in the regular method described the solution is alkaline with ammonia only, and all mono-sulphur is in the form of non-oxidisable zinc sulphide.

Experiment 1.—Following the regular method except in the matter of heating, indicates the speed of the reaction between sulphite and poly-sulphur:—

Test.	Time heated. Minutes.	No. of Mixings.	Iodine Titration.
a	15	3	39·49
b	23	2	39·56
c	60	3	39·50
d	120	3	39·45

The results indicate that the prescribed conditions make ample provision for solution of all poly-sulphur provided the full heat of the steam-bath is used. They further indicate that properly executed duplicates will yield figures in satisfactory agreement.

Since strontium sulphite could not be assumed to be absolutely insoluble it was necessary to determine a blank for sulphite reaching the stage of iodine titration.

Experiment 2.—Blanks run with 5 cc. of sodium sulphite solution gave 0·12 and 0·11 cc. N/10 iodine. A blank run with 10 cc. sodium sulphite, using 30 cc. strontium chloride, gave 0·11 cc. iodine. In each case about 2 grms. C.P. potassium iodide were added to the filtrate before titration.

Since the size of the blank was not affected by the quantity of sodium sulphite used, the blank titration must be attributed solely to the solubility of strontium sulphite and not to the presence of sodium thiosulphate as an impurity in the sample of sodium sulphite employed. Remembering that in the execution of the method in practice no correction for the end-point with starch is called for, since that is automatically provided through the necessity of subtracting the thiosulphate figure, it is fair to set for the solubility of strontium sulphite a correction of 0·10 cc. N/10 iodine per 200 cc. filtrate.

Incidentally it may be noted that we have here the basis for a good practical method for estimating thiosulphate in the presence of sulphite.

If, as the writer believes, the combined determination of mono-sulphur and poly-sulphur as described constitutes a method for the estimation of sulphide sulphur which is more accurate in practice than any other previous method it is obviously impossible to check the accuracy of the new method by comparing its results with those afforded by other methods. But such a comparison is of importance for practical reasons and has been undertaken.

Experiment 3.—Taking the standard method (Bur. of Chem., *Bull.* 152, p. 70) of the A.O.A.C. as a basis, procedure was modified in accordance with facts regarding the estimation of sulphuric acid as barium sulphate brought out by Allen and Johnston (*Journ. Am. Chem. Soc.*, 1910, xxxii., 588) and by Walter Allen and Bishop (*Proc. Eighth Intern. Congr. Appl. Chem.*, 1912, i., 33). Using 10 cc. of the diluted sample, sulphide sulphur was separated by ammoniacal zinc in the usual way. Next followed digestion with 10 cc. N/ × 10 caustic potash, adding water as needed, oxidation with hydrogen peroxide and strong acidification with 25 cc. concentrated hydrochloric acid. To remove chlorates (compare Ramsay, *Journ. Agr. Sci.*, 1914, vi., 194) and silica, which must necessarily be present from the action of alkali on glass, the solution was evaporated to dryness and the residue was heated several hours at 105 to 110° C. It was then taken up with hot water and 5 cc. concentrated hydrochloric acid, and the filtered solution, after cooling and diluting to about 700 cc., was precipitated cold with a 5 per cent solution of barium chloride through a capillary tube, according to the procedure of Walter Allen and Bishop. The next day the precipitate was filtered on paper, cautiously ashed in a platinum crucible, and ignited for thirty minutes in the covered crucible over a No. 3 Méker burner.

To determine the value of the factor S/$BaSO_4$ under these conditions, 25 cc. of N/2 sulphuric acid were precipitated after the addition of hydrochloric acid only, and after the addition of 10 cc. of N × 10 caustic potash, acidification, evaporation, &c., as in the method of analysis, and this factor was used in calculating the results. The trace of sulphur derived from the reagents was determined and allowed for in all the work. All operations were performed in duplicate.

The samples were made after different formulæ in connection with another investigation. They were diluted and analysed, using the gravimetric method for sulphide sulphur, one to three days after preparation. For the determination of the poly-sulphur figure the dilutions unfortunately were not made until between eight to ten weeks later, the concentrates being preserved meanwhile in well-filled and well-sealed bottles. It is not desired to discuss at the present time changes which may occur in lime-sulphur solutions during storage, but it is necessary to give here the results for thiosulphate sulphur also.

The results obtained appear in Table I., expressed as percentages of the diluted samples.

TABLE I.—*Results in Percentages.*

First dilution.

Sample.	Thiosulphate S.	Sulphide S. Gravimetric.	Sum.
A	0·387	1·622	2·009
B	0·458	1·674	2·132
C	0·453	1·755	2·208
D	0·418	1·801	2·219
E	0 444	1·790	2·234

Second dilution.

Sample.	Thiosulphate S.	Sulphide S. Volumetric.	Sum
A	0·378	1·644	2·022
B	0·445	1·744	2·189
C	0·443	1·815	2·258
D	0·408	1·839	2·247
E	0·440	1·819	2·259

The volumetric method for sulphide sulphur gave distinctly higher results in all cases, the actual differences varying from 0·022 per cent to 0·070 per cent. But it is evident that the thiosulphate sulphur decreased slightly during storage in all cases. If it is permissible to assume that some thiosulphate sulphur had become changed to sulphide sulphur, and comparison is made between the sums of the two forms of sulphur, the volumetric method still gives the higher results in all cases, the actual differences varying from 0·011 per cent to 0·057 per cent. The parallelism indicates a greater fault in the factors employed for calculating the results than in the rationale of either method, and since the factor $S/BaSO_4$ is purely empirical under the conditions of the gravimetric method the probability of error rests there.

No experiments have been performed upon the applicability of the method to use dipping baths contaminated with filth from animals.

Conclusions.

Methods are now available for estimating iodometrically the three important forms of sulphur in lime-sulphur solutions—thiosulphate sulphur, mono-sulphur, and poly-sulphur, thiosulphate being the substance directly titrated in each case. The methods appear theoretically sound and practically applicable. The use of a single standard solution which can be so easily and accurately prepared and used as N/10 iodine means a possibility of increased accuracy as well as a saving of time over the gravimetric estimation of sulphur as barium sulphate under conditions which demand the employment of an empirical factor.

THE ACTION OF ALUMINIUM CHLORIDE ON THE ALIPHATIC ETHERS.*

By G. B. FRANKFORTER and E. A. DANIELS.

It has been shown by Frankforter and Kritchevsky (*Bull.* 2, Chemical Studies, University of Minnesota) that aluminium chloride not only acts as a catalyst according to the well-known Friedel-Crafts reaction, but also also as a dehydrating reagent, removing a molecule of water according to the common condensation reaction. In a few cases, however, they found that it gave the aldol reaction when the halogen aldehydes, namely chloral and bromal, were brought in contact with other reacting constituents. Thus, when methyl phenyl ether is treated with chloral in the presence of aluminium chloride, the following almost quantitative reaction takes place if the temperature is kept low enough :—

$$2C_6H_5OCH_3 + OCH-CCl_3 + AlCl_3 = (C_6H_4OCH_3)_2CHCCl_3 + H_2O + AlCl_3;$$

but, when anthracene is treated with chloral in the presence of aluminium chloride, the aldol reaction takes place according to the following equation :—

$$C_{14}H_{10} + CHO—CCl_3 + AlCl_3 = C_{14}H_9CHOH—CCl_3 + AlCl_3.$$

In a very few cases aluminium chloride was found to combine directly with the reacting components forming unstable compounds.

Following out the line of work mentioned above as well as the work of Frankforter and Poppe (*8th Intern. Congr. Appl. Chem.*, 1910, xxv., 363), the aliphatic ethers were treated with chloral in the presence of aluminium chloride and finally with the chloride alone. It was soon found that the reaction with the aliphatic ethers does not proceed along the same lines as observed in the aromatic ethers. However, the reaction proved to be of considerable interest, although it was extremely complex.

The first experiments were tried with common ethyl ether and chloral in the presence of aluminium chloride. Although the conditions were widely varied, the reaction seemed extremely complex in each case and no compounds analogous to those obtained from the aromatic ethers were formed, but when commercial ether was used, a heavy, white, flocculent precipitate was formed. The formation of this precipitate which was subsequently found to be due to moisture in the ether was used as a basis for a qualitative test for water in ether.

It was thought that the complex reaction was due, partly at least, to reactions between two of the constituents, namely, aluminium chloride and chloral, or aluminium chloride and ether. Thus Combes (*Ann. Chem.*, 1887 [6] xii., 3, 199) found that chloral and aluminium chloride react on each other, forming tetrachlorethylene and a polymerised form of chloral which he called perchloral. We were unable to obtain this compound. In fact, we were unable to identify any of the compounds formed in this experiment.

The experiments which follow were carried out with perfectly dry ether, inasmuch as we found that water in the ether completely changed the reaction. In order to eliminate any possibility of moisture during the reaction, a flask was fitted with a two-hole stopper, one hole connected with a calcium chloride drying tube and the other carrying a thermometer in order to observe the temperature. The mixture of ether and chloral was placed in the flask and cooled down to 0°, then powdered aluminium chloride was added in 5 grm. portions. A large amount of heat was generated notwithstanding the fact that the flask was kept in ice-water. At the same time a small amount of hydrochloric acid was liberated and escaped through the drying tube. Aluminium chloride was added until the ether was saturated and a small quantity of solid chloride was left in the bottom of the flask. We were unable to prove that the hydrochloric acid gas liberated was not due to the action of moisture on the chloride.

It required about an hour to add the chloride. At the end of that time the solution had changed from a perfectly colourless to a straw yellow. After standing in ice-water for two hours, the flask was removed and the temperature allowed to slowly rise to room temperature. The colour changed with the rise in temperature until at 22° it was a reddish brown. The mixture was then allowed to stand over night at a temperature of 0°. In the morning the whole mass had changed to a light brown jelly. It turned darker on standing at room temperature. Treated with water a large amount of heat was liberated and the substance separated out as a thick dark brown mass. This was subjected to steam distillation when several substances were obtained, but the quantities were too small to permit a careful examination. During the distillation, there was a distinct odour of ether. The viscous insoluble material remaining in the flask after the steam distillation was filtered off and examined. It was dissolved in ether and filtered. There remained an undissolved gelatinous substance which subsequently was found to be a simple aluminium compound.

The ether extract, which carried practically all of the organic substance, left upon evaporation a dark brown resinous mass. It was distilled under diminished pressure. At 52° and 22 mm. pressure, crystals formed in the condenser, evidently chloral hydrate; at 62—80° and the same pressure, a small amount of liquid passed over, then the temperature rose to 125°, when a very small quantity of a liquid passed over, but the quantity was too small for exhaustive examination. The residue left in the flask was of a dark brown colour and appeared charred. With the hope of obtaining more satisfactory results, the above experiment was repeated, except that the temperature was kept at −8° instead of 0°. The same reaction seemed to take place although the results obtained by distillation *in vacuo* were some somewhat different. A small quantity of liquid passed over at 100°, together with a large amount of hydrochloric acid. The oil was found to react vigorously with water, and is evidently an organic compound of aluminium chloride. Crystals passed off between 110 and 135°. They were removed, pressed between filter paper and finally dried in a desiccator over sulphuric acid. They melted at 22—23° and were readily decomposed in the air, changing to a liquid. The quantity of substance, however, was not sufficient for an exhaustive examination.

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* *Journal of the American Chemical Society*, xxxvii., No. 11.

They were doubtless the compound of aluminium chloride and ether to be described later. The residue left in the flask was insoluble in ether. It was partially soluble in water with evolution of heat and a peculiar disagreeable odour. An exhaustive examination of the residue failed to yield a definite compound.

The Action of Aluminium Chloride on Ether.—It was observed early in the above experiments that aluminium chloride combined readily with ether, producing a well crystallised compound. Absolute ether was therefore treated with equal weights of anhydrous aluminium chloride at a low temperature. The solution immediately changed to a dark purple and much heat was liberated. The mixture was kept at −15° over night. In the morning the whole was a solid mass of well-defined crystals. These crystals were found to dissolve when the room temperature was reached, but reformed on cooling. They were found to react violently with water.

In going over the literature it was found that various salts of ether had been prepared. Thus titanium chloride (*Bull. Soc. Chim.*, 1880, xxxiii., 566) was found to combine with ether and to form a double salt. Tin, bismuth, zinc, arsenic, and antimony chlorides and bromides (*Journ. Pharm.*, [3], xxvi., 161; *Journ. Prakt. Chem.*, 1861, lxxxiii., 259) form double salts with ether, representing the general formula, $SnCl_4.C_4H_{10}O$ and $SbBr_3.C_4H_{10}O$.

Boeseken (*Rec. Trav. Chim.*, 1901, xx., 102), in his work on aluminium chloride, prepared an acetyl double salt by treating acetyl chloride dissolved in carbon disulphide with aluminium chloride, to which he gave the formula $AlCl_3.CH_3COCl$. Plotnikov (*Zeit. Anorg. Chem.*, 1907, lvi., 53) described a double salt of ether and aluminium bromide to which he gave the formula, $AlBr_3.(C_4H_{10}O)$ and Walker and Spencer (*Journ. Chem. Soc.*, 1904, lxxxv., 1106) in a study of the action of aluminium chloride on organic compounds containing oxygen incidentally studied the reaction between ethyl ether and aluminium chloride. They dissolved the organic substance in carbon disulphide and then added the aluminium chloride. Evaporating off the solvent by a current of dry air, they obtained large brown plates. They obtained by analysis 13·93 per cent of Al for the compound, to which they ascribed the formula $Al_2Cl_6.2C_4H_{10}O$. The theoretical for Al is 13·01 per cent.

Inasmuch as the reaction between ether and aluminium chloride, and especially the compound mentioned above, has not been carefully studied, we have given the reaction further consideration, feeling that there was still much to be learned.

Best results were obtained by using pure dry ether without a diluent and keeping the temperature fairly constant at 15° until the first few portions of the chloride had been added. After this the reaction seemed to proceed best between 35 and 50° with frequent shaking. It was also found that good fresh aluminium chloride in pieces about the size of a pea gave better results than the powdered chloride, which reacts too vigorously, resulting in more or less decomposition. The chloride dissolves slowly, forming a syrupy solution after about one and one-half times the weight of the ether has been added. On cooling the thoroughly saturated ether solution, a large amount of beautiful transparent crystals in the form of large plates separated out from an almost colourless mother liquor. They were recrystallised from absolutely dry ether several times and allowed to dry in a desiccator over concentrated sulphuric acid,

The freshly prepared crystals have a melting point of 33—35°, a little lower than the corresponding bromide. The average of several analyses for aluminium was 14·9 per cent and for chloride 50·8 per cent. The theory for the compound $Al_2Cl_6.2C_4H_{10}O$ is Al 13·01 per cent, Cl 51·3 per cent. That the results for aluminium were higher than the theory is very easily explained by the fact that these crystals are not stable and a slight loss of ether would make an appreciable increase in the percentage of aluminium. After standing for some time over sulphuric acid in a desiccator, the crystals were found to contain a higher percentage of aluminium (15·16 per cent) and a lower per cent of chlorine (50·4 per cent). They were found to be fairly stable in a desiccator over sulphuric acid, although there was a gradual loss in weight, due not only to loss of ether, but also hydrochloric acid gas. Thus, in six days, a loss of 2·7 per cent and in thirty-eight days 6·1 per cent loss was found. The compound is doubtless stable in perfectly dry air, and the loss of both ether and hydrochloric acid is due to partial hydrolysis forming basic aluminium chloride, thus liberating the ether. The odour of hydrochloric acid is noticeable if the salt is brought in contact with moist air; dissolved in water, both hydrochloric acid and ether are liberated, On evaporating this water solution to dryness and drying at 106°, the substance on analysis showed 32 per cent of aluminium and 16 per cent of chlorine.

(To be continued).

BORON: ITS ABSORPTION AND DISTRIBUTION IN PLANTS AND ITS EFFECT ON GROWTH.*

By F. C. COOK, Physiological Chemist, Bureau of Chemistry.

(Continued from p. 3).

The results with wheat grown in plots at Arlington Farm, Va., are given in Table IV. The manure was applied at the rate of 20 tons per acre. The wheat was planted in October, 1913, and harvested in June, 1914, the soil samples being tested at the time of harvesting. On the borax plot the wheat plants, which were yellow during the winter, became green and normal in appearance in the spring. The yield of wheat from the borax plot was 90 per cent of the control, but larger than that from an unmanured plot which was simultaneously tested. The amount of borax added to the borax plot was about four times that necessary to act as a larvicide, but only a trace of boron was found in the wheat grain or straw. The wheat grains were sound, and the nitrogen and ether extract results of the control differed very little from those of the wheat and straw from the borax-treated plot. A trace of boron was found in the grains and straw from the borax plot, and the borax-treated soil showed 0·003 per cent of boric acid. The soil sample from the borax plot contained more nitrates than the control sample. Nitrogen was estimated by the Kjeldahl-Gunning method, and nitrates by the method recommended by the American Public Health Association.

Results of the analyses of soybeans (*Glycine hispida*), string beans (*Phaseolus vulgaris*), and potato plants grown on plots at Arlington Farm, Va., are recorded in Table V. The roots and beans of the soybeans contained about equal amounts of boron, and rather large quantities were found in the tops of all the plants analysed. There was a more equal distribution of boron in the roots, tops, and beans of the string beans than in the case of the soybeans.

The potatoes showed only traces of boron in the tops, the largest part of the boron being found in the roots, although the tubers contained a fairly large amount. All control plants contained a little boron. The addition of lime with the borax did not prevent the absorption of boron by the plants, as much boron being absorbed from the calcined colemanite plots as from the borax plots.

In Table VI. results of the analyses of corn (*Zea mays*), wheat, peas (*Pisum sativum*), and oats (*Avena sativa*), grown on plots at New Orleans, La., and Dallas, Tex., are recorded. The entire plants, which were three months old and small, were used. The corn and wheat plants took up equal amounts of boron. Soluble boron was found in all nine samples of soil from New Orleans, while

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* *Journal of Agricultural Research*, v., No. 19, Dept. of Agriculture, Washington, D.C.

Table IV.—*Perrcentage of Boron in Wheat, Straw, and Soil. Plot Tests at Arlington Farm, Va.*

Series No.	Treatment of manure per 8 bushels.	Material.	Nitrogen.	Nitrogen as ammonia (MgO method).	Nitrogen as nitrates.	Ether extract.	Acid-soluble boron as boric acid.
1.	Two to three pounds borax added . ..	Wheat grains	2·15	—	—	1·70	Faint trace.
		Wheat straw	0·281	—	—	2·12	Do.
		Soil 3 to 4 ins. deep .	0·09	0·004	0·0018	—	0·003
2.	Control	Wheat grains	2·21	—	—	1·77	None.
		Wheat straw	0·323	—	—	2·27	Do.
		Soil 3 to 4 ins. deep .	0·09	0·003	0·0012	—	Do.

Table V.—*Percentage of Boron in Soybeans, String Beans, and Potatoes. Plot Tests at Arlington Farm, Va.*

Series No.	Treatment of soil per square rod.	Boron as boric acid (dry basis). Soybeans. Roots.	Soybeans. Tops.	Soybeans. Beans.	String beans. Roots.	String beans. Tops.	String beans. Beans.	Potatoes. Roots.	Potatoes. Tops.	Potatoes. Potatoes.
1.	1·61 pounds of calcined colemanite added ..	0·0086	0·0048	0·0092	0·0044	0·0075	0·0045	0·0170	0·0012	0·0094
2.	2·88 pounds of calcined colemanite added ..	0·0160	0·0076	0·0136	0·0083	0·0177	0·0213	0·0144	Trace	0·0021
3.	3·96 pounds of borax added..	0·0124	0·0047	0·0104	0·0086	0·0093	0·0117	0·0354	Trace	0·0066
4.	3·96 pounds of borax and 2 pounds of lime added	0·0126	0·0040	0·0164	0·0093	0·0099	0·0080	0·0165	Trace	0·0019
5.	2 pounds of lime added .	0·0030	0·0008	0·0036	0·0050	None	0·0042	Trace	None	0·0010

Table VI.—*Percentage of Boron in Corn, Wheat, Peas, Oats, and Soil. Plot Tests at New Orleans, La., and Dallas, Texas.*

Series No.	Treatment of manure per 8 bushels.	New Orleans, La. Boron as boric acid (entire plant, dry basis). Corn.	Wheat.	Soluble boron as boric acid in soil, sample taken 4 inches deep.	Dallas, Tex. Boron as boric acid (entire plant, dry basis). Peas.	Oats.	Soluble boron as boric acid in soil, sample taken 3 inches deep.
1.	0·5 lb. of borax added	0·013	0·011	0·0006	0·010	0·001	—
2.	0·62 lb. of borax added	0·015	0·015	0·0009	0·010	0·006	Trace
3.	Control	Trace	Trace	Trace	0·003	—	—
4.	0·75 lb. of borax added	—	—	0·0003	0·040	0·025	—
5.	1·25 lbs. of borax added	—	—	0·0013	0·026	0·025	Trace
6.	Control	—	—	Trace	0·0005	—	—
7.	0·75 lb. of calcined colemanite added	—	—	0·0008	—	—	—
8.	1·50 lbs. of calcined colemanite added	—	—	0·0032	—	—	—
9.	Control	—	—	Trace	—	—	—

Table VII.—*Percentage of Boron and Ash in Radishes, String Beans, Cowpeas, Peas, and Soil. Plot Tests at Orlando, Fla.*

Series No.	Treatment of manure per 8 bushels.	Radishes (dry basis). Tops. Ash.	Radishes Tops. Boron as boric acid (ash-free basis).	Radishes Roots. Ash.	Radishes Roots. Boron as boric acid (ash-free basis).	String beans (dry basis). Tops. Ash.	String beans Tops. Boron as boric acid (ash-free basis).	String beans Roots. Ash.	String beans Roots. Boron as boric acid (ash-free basis).	Cowpeas (dry basis). Tops. Ash.	Cowpeas Tops. Boron as boric acid (ash-free basis).	Cowpeas Roots. Ash.	Cowpeas Roots. Boron as boric acid (ash-free basis).	Peas (entire plant, dry basis). Boron as boric acid	Soluble boron as boric acid found in sample of soil 3 to 4 ins. deep.
1.	0·75 lb. borax added . ..	34·44	0·162	50·08	0·039	—	0·086	22·98	0·011	29·49	0·162	35·15	0·222	0·212	0·0006
2.	1·25 lbs. borax added . ..	49·49	0·226	51·12	0·087	17·56	0·080	14·89	0·015	33·22	0·140	45·68	0·240	0·229	0·0010
3.	Control . ..	45·25	0·018	45·04	0·010	22·80	0·011	—	0·007	20·18	0·024	—	0·029	0·024	0·0003

only two of the five samples from Dallas contained any. The peas absorbed more boron than the oats, especially in Series 1, 2, and 3.

In Table VII. the boron content of radish (*Raphanus sativus*), stringbean, cowpea, and pea plants, grown on borax and control plots at Orlando, Fla., is given. An appreciable amount of soluble boron was found in the soil samples from all three plots. The radish plants contained a large amount of boron in the tops, as well as an appreciable quantity in the roots. The string beans did not absorb as much boron as the radishes, but contained a large percentage of the absorbed boron in the tops. The cowpeas absorbed large amounts of boron, more being found in the roots than in the tops. The pea plants also absorbed boron in great quantities. All the control plants contained boron to a marked degree, which is not surprising, as 0·0003 per cent of soluble boron was found in the control soil sample examined at the close of the test.

As there was little rain at Orlando while these tests were being conducted, and as relatively large quantities of soluble boron were found in the samples of soil tested, it is not surprising that the plants absorbed large amounts of boron.

(To be continued).

NOTES AND QUERIES.

The Weed called "Couch"—Could anyone give information about the weed called "Couch" as to its commercial value, as I now understand that it *is* of value, and I have plenty of it for sale. Or could you put me into communication with someone who could tell me a little about it, and how to treat it?—H. M. Gledstone.

THE CHEMICAL NEWS

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THE PRESENCE OF BENZENE HOMOLOGUES IN THE HIGH BOILING DISTILLATES OF PETROLEUM.

By BENJAMIN T. BROOKS and IRWIN W. HUMPHREY.

In studying the properties of the substances which cause fluorescence in petroleum distillates (Brooks and Bacon, *Journ. Ind. Eng. Chem.*, 1914, vi., 623) the conclusion was drawn that the substances in question were probably related to benzene, and the essential facts advanced in support of this hypothesis were the following:—

(1) Oils distilled *in vacuo* are much less fluorescent than when distilled slowly at ordinary pressure and accompanied by cracking and formation of relatively large quantities of coke. There is an unmistakable parallelism between the distillation of coal *in vacuo* and at atmospheric pressure and the distillation of oil under similar conditions. In general, destructive distillation of organic material containing little oxygen is conducive to the formation of aromatic hydrocarbons. The coal-tar distillates produced by distillation *in vacuo* are relatively very low in aromatic hydrocarbons and are only very slightly fluorescent (A. Pictet, *Ber.*, 1913, xlvi., 3342; Jones and Wheeler, *Journ. Chem. Soc.*, 1914, cv., 2562; 1915, cvii., 1318.

(2) No fluorescent organic substances are known which belong strictly to the paraffin or naphthene series of hydrocarbons. The vast majority of fluorescent organic compounds whose constitution is known possess condensed ring structures, such as the derivatives of benzene, naphthalene, anthracene, fluorene, pyrone, acridine, azine, oxazine, thiazine, and the like. The character of the fluorescence of petroleum distillates is affected by such solvents as carbon bisulphide, aniline, nitrobenzene, amyl alcohol, pyridine, ether, acetone, &c., in a manner strictly parallel to the effect of these solvents on the fluorescence of the esters of terephthalic acid studied by Kauffman (*Ann.*, 1912, cccxciii., 1).

(3) Suspensoids of colloidal degree of dispersion were found to be totally absent in strongly fluorescent petroleum oils.

(4) The fluorescent substances are readily sulphonated by strong sulphuric acid, forming water-soluble compounds whose aqueous solutions are strongly fluorescent.

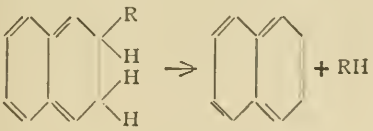
Before considering the matter further it should be recalled that all petroleums which have been thoroughly examined have been shown to contain benzene and its simpler homologues. Even gasoline distilled from light Pennsylvania crude oil contains small percentages of them. The isolation and identification of the higher benzene homologues has apparently not been attempted, probably owing to the much greater experimental difficulties encountered, although Markownikow (*Ann.*, 1886, ccxxxiv., 89) isolated 3·5-diethyltoluene and isoamylbenzene, $C_6H_5.C_5H_{11}$, from the light kerosene distillate of Baku oil and H. O. Jones and H. A. Wootton (*Journ. Chem. Soc.*, 1907, xci., 1146; *Chem. Zent.*, 1907, II., 1029) isolated β-dimethylnaphthalene from a Borneo petroleum.

Some Conditions under which Benzene Hydrocarbons are Formed.

It is known that in the manufacture of oil-gas at a temperature of about 950° profound decomposition of the oil occurs, with the formation of hydrogen, methane, acetylene, olefines, and a series of benzene hydrocarbons. The assumption is probably warranted that whenever the temperature is sufficiently high for the formation of acetylene aromatic compounds will be found among the reaction products. The lowest temperature at which acetylene can be formed from petroleum oils has apparently not been determined, but no references exist in the literature noting its presence in oil-gas made at temperatures lower than 750° (W. A. Noyes, *Journ. Am. Chem. Soc.*, 1894, xvi., 688). It is known that under certain conditions naphthenes may form benzene hydrocarbons, accompanied by the splitting off of hydrogen, and the work of Nikiforoff and Ogloblin (*Zeit. Angew. Chem.*, 1905, xviii., 546) shows that by employing heat alone temperatures of at least 525 to 550° are necessary. (Since the outbreak of the war in Europe benzene and toluene have been made from petroleum on a commercial scale in several plants using the Hall process, which method employs a temperature of about 650° and pressures of 50 to 75 lbs. per square inch, and by the Rittman process employing slightly higher temperatures and pressures). Engler ("Das Erdol," i., 574) obtained no free hydrogen whatever by heating kerosene to temperatures below 470°. Although cyclohexane and methyl cyclohexane have been converted into benzene and toluene respectively by splitting off hydrogen in the presence of metallic catalysts, such as nickel, platinum, and palladium, at temperatures below 300°, these conditions are widely removed from the conditions of the experiments described in this paper.

We have found that the heavier portions of Jennings and Oklahoma crude petroleums—*i.e.*, that part remaining after removing by distillation those fractions boiling below 275°, and hereinafter designated as reduced oil—yields benzene, toluene, and xylene by "cracking" at temperatures not exceeding 420° and under 100 lbs. pressure; that these aromatic hydrocarbons are also obtained by cracking Jennings and Oklahoma reduced oils by heating with anhydrous aluminium chloride; that pure paraffin wax on cracking under either of these conditions does not yield benzene or its homologues, nor does it yield fluorescent distillates; that synthetic phenyl-paraffin, made by condensing chloroparaffin with pure benzene, is readily cracked by heating to 420° under 100 lbs. pressure or by merely heating with aluminium chloride to 230°, yielding benzene and toluene among the reaction products. It is noteworthy, too, as agreeing with the above noted theory of the nature of the fluorescent compounds in petroleum, that while the decomposition products of pure paraffin are not fluorescent the introduction of a benzene nucleus leads to decomposition products which are highly fluorescent.

Jones and Wheeler (*Journ. Chem. Soc.*, 1914, cv., 2562) have shown that certain aromatic hydrocarbons are produced in the distillation of coal *in vacuo* at 350°, and point out that this is below the temperature at which hydrogen is split off. They suggest that a reaction of the following type may take place:—



Naphthalene.

In view of the facts recorded in this paper, we believe that the formation of free naphthalene at 350°, as noted by Jones and Wheeler, is better accounted for by the decomposition of a complex molecule containing the naphthalene radicle, in the same way as we have shown phenyl-paraffin to be broken down into benzene, toluene, and unsaturated hydrocarbons. For example—

$C_{10}H_7.C_nH_{2n+1} \rightarrow C_{10}H_8$ (naphthalene) $+ C_nH_{2n}$ (olefine of naphthene).

(In a recent paper [*Journ. Chem. Soc.*, 1915, cvii., 1582] Jones states that cyclohexane, methyl cyclohexane, and tetrahydronaphthalene began to decompose at approximately the same temperature—namely, between 490 and 510°. The gas evolved contained approximately 40 per cent hydrogen. Dihydronaphthalene decomposed at 390° and the gas evolved contained 80 per cent hydrogen. The important bearing of Jones's work upon the matter here presented is the confirmation of the earlier work that a temperature of 500° is necessary to form benzene or toluene from cyclohexane and methyl cyclohexane respectively, and that this decomposition of cyclohexane occurs relatively much easier than in the case of the normal paraffins).

Experimental Part.

The Oklahoma reduced oil employed in the following experiments had the specific gravity 0·877, 20°/4°, all material boiling below 275° having been distilled from the mixture. Three litres of the oil were cracked by slowly distilling under 100 lbs. pressure in a small iron still, capacity about 5·5 litres, the temperature gradually rising during the distillation through the range 375 to 415°. After three hours the distillate, 75 per cent of the charge, was redistilled at atmospheric pressure, and the fraction boiling below 150°, amounting to 22 per cent of the charge, was collected separately (*cf.* Brooks, Bacon, Padgett, and Humphrey, *Journ. Ind. Eng. Chem.*, 1914, vi., 180; Brooks, *Journ. Franklin Inst.*, December, 1915, p. 653). This low boiling portion was extracted at −15° with liquid sulphur dioxide. This extraction was carried out by shaking in a large Dewar flask with an equal volume of liquid SO_2 divided into three portions, which were added successively after syphoning off the heavy layer from the preceding treatment. From the sulphur dioxide solution there were recovered about 10 per cent by volume of the gasoline fraction, or 2·2 per cent of the original charge of reduced oil. This was fractioned three times, and the fractions boiling at 75 to 85°, 105 to 115°, and 135 to 145° were nitrated first in the cold and finally on a steam-bath with an excess of ordinary sulphuric and nitric acids. The crude crystalline masses obtained by pouring into water were recrystallised, and pure 1·3 dinitrobenzene, m.-p. 90°, also 2·4-dinitrotoluene, m.-p. 70°, and 2·4 6 trinitrometaxylene, m.-p. 182, were isolated.

We then examined the gasoline obtained by heating heavy high boiling oils with anhydrous aluminium chloride. Twenty litres of Oklahoma reduced oil were heated with 6 per cent anhydrous aluminium chloride until four litres of light distillate were collected. When this was extracted with one-half volume liquid sulphur dioxide 0·40 litre extract was obtained. On fractionating and nitrating the proper fractions as before, pure 1·3 dinitrobenzene, 2·4-dinitrotoluene, and 2, 4, 6 trinitro-*m*-xylene were isolated.

In order to determine quantitatively the amounts of aromatic compounds present in cracked gasolines, and in order to compare these results with those given by several natural gasolines distilled from crudes, we extracted a series of gasolines by using a total of 1·5 volumes of liquid sulphur dioxide in three successive extractions at −15° in Dewar flasks. The tabulated results (Table I.) include a sample of gasoline made by cracking Texas Solar Oil with aluminium chloride.

Relative Stability of Paraffins and Naphthenes.

In cracking commercial paraffin we were surprised to find that this material is more difficult to decompose than light lubricating oil which is composed almost exclusively of naphthenes and polynapthenes. While the simpler naphthenes whose constitutions are known, such as cyclohexane and methyl cyclopentane, are apparently more stable to heat than normal paraffins, and have been found among the products resulting from heating simple paraffin hydrocarbons under pressure (Engler), the instability of the three- and four-membered rings in the terpene series is well established. The properties of cycloheptane, cyclo-octane, cyclononane, and their derivatives are not so well known, but their tendency to rearrange to five- and six-ring systems has been frequently observed. It is probable that the relatively greater ease of cracking petroleum naphthenes, such as constitute much the greater part of light lubricating oil, as compared with the cracking of commercial paraffin wax of substantially the same average molecular weight and boiling-point range, is to be interpreted as indicating that these high boiling naphthenes belong to series other than of five- or six-membered rings. The behaviour on heat decomposition of naphthenes of known constitution, such as cyclooctane, cyclononane, or their derivatives, is not known.

That the heavy residues of certain crudes are more easily cracked than others is known to refiners. Heavy Mexican crude particularly is readily decomposed by heat and is conspicuous for its extremely high coke residue. (By slow direct fire distillation we have noted coke residues from this crude as high as 42 per cent). That higher temperatures are required for the cracking of paraffin than for reduced Jennings oil, made up of naphthenes and polynaphthenes and free from paraffin and from which all constituents boiling below 275° had been removed, was shown in two parallel distillations made under 100 lbs. pressure, the temperature being taken about ten minutes after distillation had commenced and afterwards at intervals of one hour (Table II.).

The summarised results in Table III. show that when anhydrous aluminium chloride is used commercial paraffin wax decomposes much less readily than the other hydrocarbons studied.

The Cracking of Synthetic Phenyl Paraffin.

A mixture of phenyl paraffins was made by condensing pure benzene with chlorinated paraffin in the presence of anhydrous aluminium chloride at moderate temperatures, not exceeding 90°. In making up this material the commercial paraffin wax, m.-p. 53°, was considered as a mixture of hydrocarbons of the mean molecular formula $C_{24}H_{50}$. Two kilogrms. of melted paraffin were chlorinated until the gain in weight was 251 grms., theoretical for $C_{24}H_{49}Cl$ being 201 grms. This was treated with two litres of pure benzene, a large excess, and 0·5 litre of carbon bisulphide. Anhydrous aluminium chloride was then added in small portions until 150 grms. had been added. The evolution of hydrogen chloride was very rapid at first, but after standing at room temperature for fourteen hours had nearly ceased. The reaction mixture was then gently warmed for six hours on a steam bath, after which time it was washed several times with hot water to remove aluminium chloride and then distilled with steam until liquid ceased to distil, the CS_2 and excess benzene being thus completely removed. After separating from water the product was heated several hours in a large porcelain dish until all emulsified water had been driven off, and then finally heated to 250° to ensure the complete removal of free benzene. The dried material was then divided into two portions, one portion of 500 grms. being heated with 35 grms. anhydrous Al_2Cl_6 to temperatures within the range 200 to 240°, the distillate being partially refluxed through a fractionating column. In three hours 78 cc. of distillate were collected. This was redistilled and 55 cc. of benzene, b.-p. 79 to 85°, and 11 cc. toluene, b.-p. 105 to 115°, were obtained.

The identity of the benzene and toluene was further proved by conversion into the corresponding dinitro derivatives. The dinitrobenzene obtained after recrystallising melted at 90° and the dinitrotoluene at 70°. Since pure benzene of tested purity and free from toluene was employed for the synthesis the presence of toluene can be accounted for only by the splitting of the phenyl paraffin, $C_6H_5CH_2 \mid CH_2R$. In this reaction the higher boiling portion of the material was converted into a mixture of naphthenes. After pouring off the warm residue from the aluminium chloride and pitch the oil was chilled and about 32 grms. of crystalline paraffin were filtered from it. The filtered oil was then a viscous material resembling light lubricating oil but possessing an *intense green fluorescence*, resembling very closely the highly fluorescent oil obtained

Table I.—*Comparison of Natural Gasoline and that Obtained by Cracking with Respect to Aromatic Compounds.*

Gasoline source.	Volume of sample treated, cc	Per cent soluble in SO_2.	Fractionation of SO_2 Soluble portion, per cent. to 90 C.	90—120° C.	120—145° C.	Grms. dinitro-toluene.	Grms. trini-troxylene.
Bristow crude	1000	4·5	9·0	48·8	17·7	1·6	—
Muskogee crude (*a*)	1000	13·0	6·1	42·3	23·0	4·1	17·4
Mexican crude..	1000	14·0	31·4	27·1	17·1	0·9	—
California crude	750	13·0	20·0	58·0	19·0	4·4	—
Texas solar oil by $AlCl_3$ ..	1000	32·5	23·0	26·1	16·9	13·8	39·6

(*a*) That the extraction of aromatic hydrocarbons by the SO_2 method, as carried out above, was incomplete was shown by the isolation of 5 grms. of dinitrotoluene after nitrating the 100 to 120° fraction of the portion insoluble in the sulphur dioxide.

Table II.—*Distillation of Paraffin and Jennings Reduced Oil under Pressure.*

Material distilled.	Time required for distillation. Hours.	Temperature at one-hour intervals.	Per cent of charge distilled at last temperature reading.	Product distilling below 150°—percentage of original charge.	Volume of gas evolved per one-litre oil.
Jennings reduced oil ..	3·5	370—415—422°	69·0	19·0	31·36
Paraffin	3·5	417—432—437°	71·0	20·5	9·33 litres

Table III.—*Decomposition of Paraffin and Naphthenes with Aluminium Chloride.*

Material treated.	Temperature when first drop distilled and at one-hour intervals.				Time heated. Hours.	Yield of product, per cent. Blg. to −150°.	Per cent Al_2Cl_6.
Jennings reduced oil	200°	226°	244°	255°	4·5	22·2	7·0
Texas solar oil	175°	190°	194°	210°	4·5	24·5	7·0
Paraffin	205°	235°	276°	282°	4·5	4·5	7·0
Phenyl paraffin	185°	220°	255°	265°	4·5	15·0	7·0

by treating Mexican crude petroleum with a small amount of aluminium chloride.

Two and one-half kilogrms. of phenyl paraffin prepared as above were subjected to distillation under 75 lbs. pressure for three hours. The 1510 cc. of distillate were redistilled, giving the following:—

Table IV.—*Results of Distilling Phenyl Paraffin under 75 lbs. Pressure.*

Fraction of product.	Quantity, cc.	Result on nitration.
70—100°	112	25 grms. crude dinitrobenzene
100—115°	150	41 ,, ,, dinitrotoluene
115—145°	272	

The isolation of dinitrotoluene, melting-point of recrystallised product 69·2°, from the products of the distillation of phenyl paraffin under pressure, shows, as in the case of decomposition by aluminium chloride, that the phenyl paraffin can break down so as to give not only benzene but toluene and possibly other homologues.

As regards the character of the fluorescent hydrocarbons in petroleum it was noted that the residue from the distillation of pure paraffin was not fluorescent, although if the distillation had been carried further, so as to form considerable coke, the oil residue would undoubtedly have been fluorescent.

Summary.

(1) Benzene and toluene and *m*-xylene have been found among the products from the cracking of heavy petroleum oils by (*a*) distillation at temperatures not exceeding 420° and pressures not exceeding 100 lbs., and (*b*) heating with anhydrous aluminium chloride to temperatures not exceeding 300°.

(2) Commercial paraffin wax does not yield benzene, toluene, or xylene under the conditions just named.

(3) Synthetic phenyl paraffin, made from pure benzene and chlorinated paraffin, yields benzene and toluene among the reaction products under the conditions named in (1).

(4) From the above facts the conclusion is drawn that the heavy high boiling fractions of petroleum contain homologues of benzene or hydrocarbons containing the benzene nucleus.

(5) The high boiling residues from the decomposition of phenyl paraffin are highly fluorescent, which supports the theory advanced in an earlier paper that the fluorescence of petroleum oils is due to the presence of complex hydrocarbons related to benzene.—*Journal of the American Chemical Society*, xxxviii., No. 2.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF TUNGSTEN.

By M. L. HARTMAN, Professor of Chemistry South Dakota School of Mines, Rapid City, South Dakota.

The directions for making the qualitative reduction test are as follows:—Boil at least 0·2 grm. of finely divided material in a small test-tube with concentrated hydrochloric acid until about one-half of the acid is evaporated. Dilute with an equal volume of water, add a piece of metallic tin, and heat if necessary. A fine blue colour in the solution, or a blue residue, indicates the presence of tungsten. If this test gives negative results, about 0·5 grm. of the material should be fused in at least 4 grms. of sodium carbonate. (This may be done with an ordinary Bunsen burner in a metal crucible or before the blast in a porcelain crucible). Dissolve the fused mass by boiling water in the crucible. Acidify the aqueous solution with an equal volume of concentrated hydrochloric acid, add a piece of metallic tin, and warm if necessary. The volume of the solution should not be more than 10 to 20 cc. A fine blue colour in the solution or a blue residue indicates the presence of tungsten. In either case, if reduction is continued long enough, a brown colour is obtained.

These tests if properly used will show the presence of tungsten in materials as low as 2 per cent, and by using special precautions will detect tungsten in even lower grade materials.

Columbium (Niobium) is the only element at all likely to give a blue colour under the conditions of this test. This blue can be distinguished from the blue of tungsten oxides by the fact that it disappears when the blue solution is diluted with water. Vanadium also gives a blue colour when solutions of its salts are reduced, but tartaric acid will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum on reduction goes through a series of colour changes from violet to blue to black. Titanium gives a violet colour. No other elements will ordinarily interfere with the test for tungsten.

The following three methods are the ones in most common use for the quantitative determination of tungsten in ores. The first two are quoted from A. H. Low's "Technical Methods of Ore Analysis." The third is a method preferred by some analysts.

Hydrofluoric Acid Method.—Treat 0·5 grm. of very finely powdered ore in a small platinum dish with equal parts of strong HCl and HF acids. Digest on a water-bath until solution is complete, adding more of each acid from time to time if necessary. It may require from one to several hours to effect complete decomposition of the ore. Usually a perfect solution may be obtained. Any tin oxide present will be unaffected. Finally, evaporate to about 15 cc. with an excess of HCl. A yellow precipitate of H_2WO_4 may separate during the final evaporation, owing to the expulsion of the hydrofluoric acid that holds it in solution. This will do no harm, provided it can be removed from the dish. Transfer the solution and any precipitate to a 6-oz. flask; add 20 cc. HCl acid and 8 cc. strong nitric acid. Boil down to about 10 cc. This will expel any remaining HF and precipitate the tungsten as tungstic acid. Dilute with 50 cc. hot water and allow to simmer at a gentle heat for about half an hour or until the tungstic acid has settled clear. Filter, wash with hot water slightly acidulated with HCl, and then dissolve the tungstic acid on the filter by pouring warm dilute ammonia over it, using as little as possible, and washing the filter with the same solution. Receive the filtrate in a weighed platinum dish. Evaporate the solution on a water bath to dryness, and then ignite the residue at a red heat, cool and weigh as WO_3. The cold residue should be a bright yellow colour. Multiply the weight of the WO_3 by 0·793 to obtain the weight of tungsten, from which the percentage in the ore may be calculated.

Fusion Method for Tungsten Ores.—Fuse 0·5 grm. of the very finely ground ore with 2 to 3 grms. of sodium-potassium carbonate in a platinum crucible for from one-half to three-quarters of an hour. Dissolve the fused mass in boiling water. The tungsten goes into solution as sodium or potassium tungstate, together with alkali silicate, and also stannate, if tin is present. The residue contains the iron, manganese, calcium, and magnesium. Filter and wash with hot water. Rinse the residue into a beaker, and warm with dilute HCl. If gritty particles remain undissolved, filter them off through the filter last used and wash with hot water. Dry and ignite the residue, and again fuse it with the mixed carbonates. Dissolve the fused mass as before, filter and unite the filtrate with the first filtrate.

Having thus obtained an aqueous solution of alkali tungstate, add to it an excess of nitric acid, and evaporate to dryness on a water-bath. Again add a little nitric acid and evaporate to dryness a second and third time. Finally heat the residue in a drying oven at 120° C. for some time and then moisten with strong nitric acid and allow to stand for fifteen or twenty minutes. Now add a hot 5 per cent solution of ammonium nitrate and filter the mixture, washing well with ammonium nitrate solution slightly acid with nitric acid to remove all the sodium and potassium salts. Finally wash once or twice more with a hot, very dilute ammonium nitrate solution and then dry the filter and contents and transfer the latter as completely as possible to a weighed platinum crucible. Moisten the paper with a strong solution of ammonium nitrate, dry it and incinerate over the crucible in a coil of platinum wire. Ignite the whole, now, with free access of air. If the tungstic acid is not pure yellow when cool, moisten with a few drops of nitric acid and repeat the ignition.

The ignited tungstic acid may contain silica and stannic oxide. The former may be removed by warming with a few cc. HF, evaporating to dryness, and igniting. The residue consists of pure tungstic acid or tungstic acid and stannic oxide. The amount of the latter is usually so small as to be negligible. If desired, the tin may be volatilised as stannic chloride by ignition with ammonium chloride. The stannic chloride is decomposed by the moisture of the air and stannic oxide may be deposited on the outside of the crucible. To prevent this, place the crucible in a larger one, and keep the outer crucible covered until the ammonium chloride is completely expelled. Now heat the inner crucible with free access of air until its contents become of a pure yellow colour. Cool and weigh. Repeat the ignition with six or eight times as much ammonium chloride as there is precipitate, until the weight of the residue WO_3 becomes constant. The tungstic oxide becomes dark on igniting in the absence of air and only assumes its true colour and weight on igniting with free access of air.

The weight of the WO_3 multiplied by 0·793 gives that of the tungsten.

Aqua Regia Method.—One grm. of the finely ground ore is treated with about 50 cc. aqua regia in a four ounce flask. The solution should be heated but not boiled, and the flask should be frequently shaken. When the solution is evaporated to 10 or 15 cc. it is diluted with 50 cc. hot water and allowed to stand for a half hour. The solution is then decanted through a filter paper, and the residue washed several times by decantation, using about 50 cc. hot water each time. The wash water should be slightly acidulated with hydrochloric acid. Add about 20 cc. ammonium hydroxide solution to the residue in the beaker, and when the yellow tungsten acid is dissolved, decant through the filter paper. The ammonium hydroxide solution is best made by adding 200 cc. strong ammonium hydroxide with 1000 cc. water and adding a little hydrochloric acid (about 10 cc.) to form some ammonium chloride. The residue is transferred to the paper by means of this solution, and washed thoroughly. The silica should be white. If it showed signs of incomplete decomposition before transferring to the paper, it should be heated with aqua regia again and treated as before. The ammoniacal solution is evaporated to dryness in a weighed platinum dish, ignited gently to drive off the ammonium salts, and finally heated strongly in the burner flame. Cool, moisten with hydrofluoric acid, and again evaporate to dryness, ignite, and weigh as tungstic oxide.—*Pahasapa Quarterly.*

THE IODIDE METHOD APPLIED TO THE DETERMINATION OF COPPER IN THE PRESENCE OF TIN.

By ROBERT W. COLTMAN

In the determination of copper in a copper-tin alloy, the usual procedures involve a separation of the copper and tin. The most common method is to decompose the alloy with nitric acid, whereby metastannic acid and copper nitrate are formed. The tin precipitate is filtered off, and the copper determined in the filtrate. This method has the disadvantage that the metastannic acid filters with difficulty; furthermore, the tin precipitate always contains traces of other metals present in the alloy, so that it must undergo further treatment.

Tin and copper may also be separated by sodium sulphide in alkaline solution, whereby the copper separates as sulphide and the tin goes into solution as a sulpho-salt. The inconvenience of this method needs no comment.

Having had occasion to investigate the behaviour of metallic copper and metallic tin when treated with concentrated sulphuric acid, the writer was struck by the facility with which the tin was held in solution. The fact that tin goes into solution as a stannic salt when treated with concentreted sulphuric acid is made use of in Low's method for antimony in babbit metal (*Journ. Am. Chem. Soc.*, 1907, xxix., 66); the hydrochloric acid added after the decomposition of the alloy ensures the tin and antimony remaining in solution after dilution. It was found that the solution of tin in sulphuric acid alone was fairly stable, and with the knowledge that stannic salts do not liberate iodine from a solution of potassium iodide, the question naturally arose as to whether copper might not be determined by the iodide method in a solution containing tin. Further experiments showed that this was quite feasible; by proper treatment of the alloy a solution of stannic and cupric sulphate in sulphuric acid may be obtained that may be titrated for copper with the same accuracy as a copper sulphate solution alone.

Although hydrochloric acid holds tin in solution much more readily than sulphuric acid, its use was not considered, as copper is not readily soluble in hydrochloric acid, and thus would necessitate the use of aqua regia to effect solution of the alloy. The nitric acid would then have to be removed by repeated evaporations with hydrochloric, consuming much time, and making the method much less simple than in its present form.

Preliminary work showed that the best method of preparing the solution was to treat the finely-divided alloy with nitric acid until decomposed, and then fume with sulphuric acid over an open flame (using a Jena Erlenmeyer). The metastannic acid dissolves to stannic sulphate, and the copper nitrate is converted into copper sulphate. On taking the cold residue up with water a clear solution is obtained that may be titrated directly for copper by the iodide method.

The use of sulphuric acid alone to decompose the alloy is not satisfactory, as a small residue of copper remains even after repeated fuming. A large excess of acid must be used, otherwise the pasty mass will spatter. It is practically impossible to control the amount of free sulphuric acid present, and this is important, as in using a mineral acid in the copper iodide method the acidity must be low.

The allowable amount of tin present under given conditions of acidity was determined as follows:—

The volume of the solution to be titrated having been chosen as 75 cc., and the amount of concentrated sulphuric acid as 3 cc., increasing quantities of metallic tin were dissolved in nitric acid, evaporated with 3 cc. of concentrated sulphuric (see Note), diluted to 75 cc., and the stabilities of the different solutions compared.

(NOTE.—Three cc. of concentrated sulphuric acid is the maximum amount which may be present in the copper iodide method, according to Gooch and Heath, *Zeit. Anorg. Chem.*, 1907, lv., 129).

Tin. Grm.	Vol. Cc.	Conc. H_2SO_4. Cc.	Remarks.
0·05	75	3	No change in one hour.
0·1	75	3	Slight turbidity in fifteen minutes.
0·2	75	3	Would not dissolve to clear solution.

It is evident that not more than 0·1 grm. of tin may be present, otherwise hydrolysis and precipitation of stannic hydrate take place in a short time.

The weight of copper titrated may be as high as 0·25 grm. (=39·3 cc. N/10 $Na_2S_2O_3$). This weight of copper in the presence of 0·1 grm. tin would be equivalent to 71·43 per cent Cu. There would then be 28·57 per cent Sn. As the amount of tin in a bronze is seldom so high as this, there is no danger that the sample taken for analysis will contain more than the allowable weight of tin, provided the amount of copper present is not much over 0·25 grm.

Experimental Data.

Standardisation of Thiosulphate Solution against Copper-foil.—The sample was dissolved in nitric, fumed with 3 cc. concentrated H_2SO_4, allowed to cool, 25 cc. water added, and evaporated again to fuming. The solution was allowed to cool, diluted to 75 cc., 10 cc. of 40 per cent KI solution added, and titrated with the thiosulphate solution.

No.	Grms. copper.	Cc. $Na_2S_2O_3$.	1 cc. = grms. Cu.
1.	0·2655	42·37	0·006266
2.	0·2648	42·24	0·006269
3.	0·2684	42·83	0·006267
Average value 1 cc. $Na_2S_2O_3$			0·006267

Titration of Copper in presence of Tin.—The solution was prepared as before, but metallic tin was added to the copper samples:—

No.	Weight (grms.).		Per cent.		Cc. $Na_2S_2O_3$.	Grm.	Cu found. Per cent.	Diff. Per cent.
	Cu.	Sn.	Cu	Sn.				
1.	0·2526	0·0311	89·04	10·96	40·31	0·2526	89·04	—
2.	0·2507	0·0504	83·26	16·74	40·02	0·2508	83·30	+0·04
3.	0·2455	0·0799	75·45	24·55	39·15	0·2454	75·41	−0·04

These differences lie entirely within the limits of error.

Analytical Procedure.

Weigh out a sample containing not over 0·25 grm. copper, and boil with 15 cc. of 2 : 1 nitric in a 500 cc. Jena Erlenmeyer provided with a small funnel to prevent loss. When the alloy is thoroughly decomposed, add dilute sulphuric acid equivalent to 3 cc. of concentrated acid, remove and rinse the funnel, and evaporate over an open flame. As the evaporation progresses, the solution becomes more and more clear. After the nitric acid is all driven off, and the sulphuric begins to fume, the stannic and cupric sulphates suddenly separate out, forming a very characteristic crystalline mass of pearly scales somewhat resembling manganese ammonium phosphate. The flask must be removed from the flame immediately after this crystallisation takes place or the mass will spatter. After cooling, take up with about 25 cc. water, shake until dissolved, and again evaporate just to fuming in order to remove the last traces of lower oxides of nitrogen. Allow to cool, take up with 50 cc. cold water (the stannic sulphate dissolves more quickly by using less water at first), and when all is in solution add 25 cc. more water, 10 cc. of 40 per cent KI, and titrate immediately with the N/10 thiosulphate. If the alloy contains a small amount of lead some lead sulphate remains undissolved, and the solution at the end-point is yellowish (owing to the lead iodide) instead of the creamy white of cuprous iodide, but the presence of lead has no effect upon the titration, at least in moderate amounts.

A copper-tin alloy containing about 10 per cent of tin and 8 per cent lead analysed as follows:—

No.	Sample. Grm.	Cc. $Na_2S_2O_3$.	Cu found.		Average per cent Cu.
			Grm.	Per cent.	
1.	0·3127	39·49	0·2474 (8)	79·14	79·16
2.	0·3227	40·79	0·2556 (3)	79·22	
3.	0·3303	41·70	0·2613 (4)	79·12	
4.	0·3108	39·21	0·2457 (4)	79·06	79·11
5.	0·3327	42·02	0·2633 (4)	79·15	

In the analyses indicated as 4 and 5 above, the alloy was decomposed with nitric, the metastannic acid filtered off, and the copper determined in the filtrate after evaporation with sulphuric.

Too much stress cannot be laid upon the fact that a second fuming of the solution is necessary; 0·05 grm. of metallic tin, treated with nitric, fumed *once* with sulphuric, and diluted to 75 cc., gave a blue colour with KI and starch requiring 0·55 cc. to discharge it. When this same amount of tin was fumed *twice* potassium iodide and starch gave no colour in the diluted solution.

As regards the time necessary Determinations 1, 2, and 3, cited above, were run in one hour. The filtering, washing, and evaporating necessary when the ordinary method was used, made the time about five hours. (In this no correction was made for any copper remaining with the metastannic acid).

The method proposed is simple, accurate, and rapid; the advantages of carrying out the analysis in the same container are obvious.

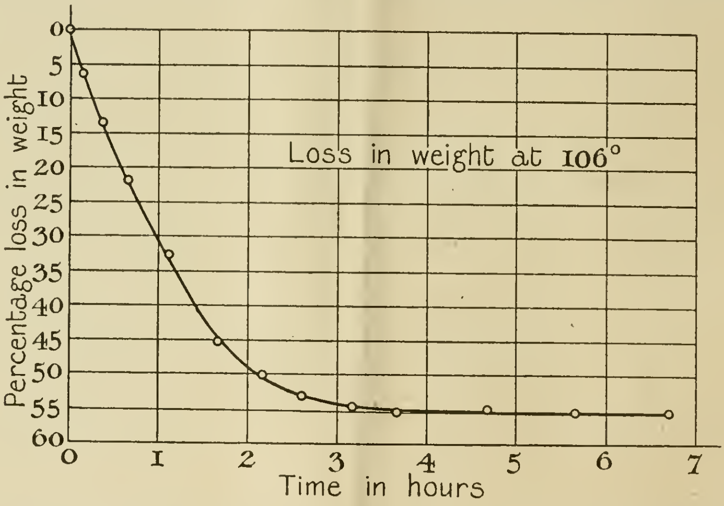
In conclusion, it must be remembered that no metals which separate iodine from potassium iodide may be present, such as antimonic or ferric salts; the method has naturally the limitations of the iodide method in this respect. It is simply the desire of the writer to show an extended use of this excellent method, thus making it available under apparently adverse conditions.—*Journal of Industrial and Engineering Chemistry*, vii., No. 9.

THE ACTION OF ALUMINIUM CHLORIDE ON THE ALIPHATIC ETHERS.*

By G. B. FRANKFORTER and E. A. DANIELS.

(Concluded from p. 23).

It is interesting to note, as is shown by the curve (Plate 1) that the original crystals when heated to constant weight at 106° showed a loss in weight of 55 per cent, and the residue when analysed gave practically the same percentage (32·85 per cent Al, 17·27 per cent Cl) of aluminium and chlorine as that obtained from the water-soluble residue. It is evident, therefore, that a basic aluminium salt is formed, probably a mixture of the approximate formula $3Al(OH)_3.2Al(OH)_2Cl$.



On exposure to the air the crystals changed first to a liquid, then a scum formed on the surface, later the whole mass became a solid of a slightly yellow colour. The material gains in weight gradually, then loses, and finally the weight fluctuates with atmospheric conditions. Thus in one case a maximum increase in weight of 17·9 per cent was noted after exposure to the air for twelve days. This then gradually lost in weight until after twenty-eight days, an increase of only 7·3 per cent of the original was noted. If the crystals are exposed to moist air over water in a desiccator a very rapid increase in weight took place. Thus, in one instance the crystals gained 11·6 per cent in weight in eight hours, 38·1 per cent in twenty-nine hours, and 238 per cent in fifteen days. The water absorbed caused a loss of hydrochloric acid and probably of ether. Chlorine was determined and a loss of about 5 per cent was found.

Normal propyl ether was substituted for ethyl ether and the properties of the additive compound studied. This compound is apparently a liquid, red in colour and not as reactive toward water as the ethyl ether addition product. The excess of propyl ether was evaporated from it by a current of dry air and the aluminium and chlorine determined. The percentages found were 15·73 per cent Al and 42·61 per cent Cl. The theory for the compound $Al_2Cl_6.2C_6H_{14}O$ is 11·5 per cent Al and 45·16 per cent Cl. Our analyses correspond closely enough with the theory considering the properties of the compound, to assume this formula. Further work on this and other aliphatic ethers is being continued in the laboratory.

Qualitative Test for Water in Ether.—In the early part of our research it was found that any solvent not entirely free from water, added to the solution of aluminium chloride in ether, would give a distinct cloudiness or precipitate. We base our test for water in ether on the fact that anhydrous aluminium chloride will dissolve in absolutely dry ether, the solution remaining clear all the time. But, if there is present a trace of water, the solution of the chloride is accompanied by the formation of a cloud or a precipitate. We assumed that the aluminium chloride is hydrolysed by the water forming a basic aluminium chloride which is insoluble in ether.

A thorough search of the literature shows that aluminium chloride has never before been used, so far as we have been able to find, for the detection of water in ether, and that the test which we propose is by far the most delicate, convenient, and practical of any now in use.

The procedure found to be best is given below. Five to 10 cc. of the ether to be tested are placed in a dry test tube and the tube closed with a rubber stopper. This is then cooled to about 10° by ice or running water, a piece of fresh anhydrous aluminium chloride of the size of a kernel of wheat dropped in, the tube again stoppered and observed with a black background. As the ether warms to room temperature, a reaction takes place, evidenced by the formation of small bubbles which rise to the top of the liquid, carrying with them, in the presence of water, a delicate white cloud, which, if present in large enough amount, will spread out as a milky layer near the top of the ether.

The density of the cloud, of course, depends upon the amount of water present. If there is an appreciable amount present, the precipitate remains permanent on shaking. This cloud, if present in small amount, is soluble or coagulated if too much aluminium chloride is present, if the solution is agitated, and thirdly, if the reaction is allowed to proceed at too rapid a rate.

The test is rendered obscure by the presence of alcohol in comparatively large amounts; thus, 7 per cent of absolute alcohol will cover up the tests entirely, while 5 per cent does not. Alcohol present in ether in this amount can readily be detected by the hydrogen evolved upon the addition of metallic sodium. Moisture of the air does no affect it, as the exposure to air is very short. Ether, direct from chemical houses, in every case shows a positive test. Ether dried over calcium chloride always gives a positive test. Ether which had been allowed to stand over metallic sodium, refluxed and distilled until moisture was proven absent by the above test, was placed in a glass-stoppered bottle which was opened only occasionally and allowed to stand for several weeks. It gave at the end of this time a positive test. This proves that anhydrous ether like practically every other absolutely dry substance is hygroscopic.

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* *Journal of the American Chemical Society*, xxxvii., No. 11.

The test is intended to prove the complete dehydration of ether by sodium and has been found delicate enough to detect one drop of water in 500 cc. of ether which had been freshly distilled over sodium.

Conclusions.

1. No definite products could be isolated from the reaction between chloral and ether in the presence of aluminium chloride.
2. The compound, $Al_2Cl_6.2HC_4H_{10}O$, an addition product of ethyl ether and aluminium chloride, has been prepared and its physical and chemical properties studied.
3. The addition product of aluminium chloride and normal propyl ether, analogous to the ethyl ether compound, has been prepared and described for the first time.
4. A new qualitative test for water in ether has been proposed and is thought to be very satisfactory and quickly made - *Journal of the American Chemical Society*, xxxvii., No. 11.

PETROLEUM REFINING.*

By ANDREW CAMPBELL.

In this paper an account was given of the process of petroleum refining, the "straight" process only being described and not those methods which involve "cracking." The selection of a process and plant depends upon two factors—the character of the crude material and the market for the products. Refining operations may be divided into three stages – (i) Distillation, (ii) Paraffin extraction and refining, (iii) Chemical treatment. In the crude oil distillation a new departure is the film still invented by Mr. M. J. Trumble. In it the crude oil is heated in pipes or retorts in a primary furnace, the hot gases from which are used to heat the vertical cylinder which forms the distillation chamber. The oil enters at the top and passes through perforated plates and is diverted by an imperforate plate so that it flows down the sides of the still in a thin film. When 60 to 70 per cent, including all the benzine, kerosene, and perhaps the intermediate fractions, are to be removed the crude oil is frequently distilled in a series of continuous cylindrical stills, the best known system being that invented by Mr. Norman M. Henderson. The crude oil after passing through a preheater is raised to distillation temperature in the first still, then passes to the second still, where it is raised to a higher temperature, and so on until it reaches the point where all the benzine, kerosene, and intermediate distillates are removed. The residue from the last still is led to one or other of a series of coking or pitch stills, where the distillation is completed. The kerosene is redistilled in stills similar to those employed for the crude oil, while for the redistillation of benzine superheated steam is used. For paraffin extraction the oil is freed from water and cooled, either by brine circulation or by the direct action of a refrigerating agent. The crude scale is then separated from the frozen mass by pumping through filter presses. Another process for the separation of paraffin from paraffin-oil mixtures was patented by the Triester Mineralöl Raffinerie and introduced into this country by Mr. von Groeling. It depends upon the fact that when a mixture of paraffin and oil is cooled down uniformly, being meanwhile kept at rest, precipitation of paraffin crystals ensues. The cooling is carried out in a water-cooled tank which is fitted with a false bottom of gauze. The crude scale thus obtained still contains heavy oil, which is removed by the process of "sweating," which consists essentially of cooling and heating alternately, the sweatings being run off and fractionated, and the process is repeated until the residue has the required melting-point. To remove the last traces of colouring matter some decolorising agent such as charcoal or bauxite must be used. An important method of refining petroleum has been worked out by Dr. Edeleanu, who removes the impurities in kerosene by dissolving them in liquid sulphur dioxide at – 10°.

BORON:
ITS ABSORPTION AND DISTRIBUTION IN PLANTS AND ITS EFFECT ON GROWTH.*

By F. C. COOK, Physiological Chemist, Bureau of Chemistry.

(Concluded from p. 24).

Discussion of Experimental Work.

It apparently made little difference in the quantities of boron absorbed by the various plants whether it was added to the manure used on the soil in the form of calcined colemanite or as borax. The addition of lime to the borax also showed no definite action in preventing the absorption of boron, although with beets (Table I.) and with one series of tomatoes (Table II.) such a reduction is indicated where the largest application of lime was made. Most of the plants analysed took up boron in proportion to the amounts present in soluble form in the soil.

The leguminous plants, which were most easily injured by boron, absorbed larger amounts than the other plants tested, while wheat and oats absorbed but little boron. It is particularly noteworthy that the wheat grown at Arlington Farm, Va., on soil fertilised with manure heavily treated with boron showed only traces of boron in the grain and straw. Haselhoff (7) found boron in the stalk of maize, but not in the grain.

The most striking differences in the absorption and distribution of boron are shown by the leguminous plants, where a more even distribution between roots, tops, and fruit is found. Potatoes also showed rather a large quantity of boron in the roots and tubers, but only a small amount in the tops. Succulent plants like beets also absorbed boron. On the other hand, tomatoes and wheat showed only traces of boron in the fruit and but little in the roots. Agulhon (1) has investigated the action of boric acid on wheat, using synthetic sterile liquid media, including both soil and water cultures. He recommends 0·0022 per cent of boron to obtain the best growth. In these tests, when borax was added at the rate of 0·62 pound to each 8 bushels of manure and this manure applied to the soil at the rate of 15 tons per acre, 0·0015 per cent of boron was added to the soil

The fact that all control plants contained a little boron shows the wide distribution of boron in the soil. From the large amounts taken up by the control plants grown at Orlando, Fla., it appears that the soil there contains more than the soil at Dallas, Tex., New Orleans, La., or Arlington Farm, Va.

The ash results of the various portions of the plants analysed vary considerably, and the variations are not in a definite direction.

A spotting or yellowing of the leaves of plants, which was first noted by Hotter (9) and later reported by several investigators, was observed in these experiments when boron was present in the soil to any extent. In the case of the tomato plants (Table II.), a yellowing of the leaves was noted when borax was used at the 0·75 pound rate, but the yield was unaffected. In some of the legumes—namely, string beans, soybeans, and peas—a noticeable yellowing of the leaves was observed when borax was added at the rate of 0·75 pound, and in these cases a reduction in stand took place. The wheat plants grown at Arlington Farm on the plot fertilised with manure treated with from 2 to 3 pounds of borax to each 8 bushels, as noted on p. 24, were yellow during the first three or four months of growth. When the growth started in the spring, however, the plants became green, and the yield of the grain was 90 per cent of the control yield, more than that obtained from the unmanured control plot. The yellowing of the leaves is an unmistakable sign of injury, although in some cases the plant can recover, or at least is not sufficiently injured to cause a reduction in the yield.

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* Abstract of Paper read at the Meeting of the Royal Society of Arts, May 16, 1916.

* *Journal of Agricultural Research*, v., No. 19, Dept. of Agriculture, Washington, D.C.

Haselhoff (7) states that the action of boron is more marked on beans than on oats or corn, and that it can be seen when small amounts of boron are present in the soil and when no action injurious to plant growth is evident. He says further that small amounts of boron stimulate the growth of beans and corn, while large amounts produce injury. In his experiments beans absorbed boron in proportion to the amount present in the soil up to a certain limit. The plants examined by Haselhoff contained from 0·04 to 0·17 per cent of boron, which is more than was found in these experiments, with the exception of the plants grown at Orlando, Fla. (Table VII.). He suggests that for safety the amount of boron in the soil be less than 0·0001 per cent. According to Brenchley (5), peas are stimulated by relatively high concentrations of boric acid, but with larger applications of boric acid the toxic action was well marked on the leaves, which tend to become brown and to die in a characteristic manner.

There is some evidence in the literature to indicate that small amounts of boron stimulate plant growth. Brenchley (5) states that below a certain dilution boron tends to produce stronger roots and shoots. Large amounts of boron are known to be toxic to practically all plants, with the exception of certain fungi.

In these experiments, where in most cases more boron was added than was necessary to act as a larvicide, no stimulating action was noted. On the contrary, an injurious action was seen with leguminous plants, which became yellow and did not show a good stand. Tomatoes, beets, lettuce, potatoes, radishes, corn, oats, and wheat appeared normal when grown in the presence of amounts of boron which produced injury to leguminous plants. When borax is added to manure at the rate of 0·62 pound to each 8 bushels and the manure is applied to the soil at the rate of 15 tons per acre, 0·0011 per cent of boron is added to the soil. This quantity of boron may injure leguminous plants, but did not injure the other plants tested, although no stimulation was noted. If the borax-treated manure is mixed with untreated manure, as would be done in many cases, since it is necessary to treat manure with borax to destroy fly larvæ during only a portion of the year, it is possible that the percentage of boron would be sufficiently reduced to bring about a stimulating action on plant growth.

In connection with the stimulating action of boron, it may be mentioned that nitrites and nitrates were detected in three or four borax-treated manure piles at New Orleans (6, p. 19), while the corresponding control piles contained no nitrites or nitrates, and several soils fertilised with borax manure have shown more nitrates than the check soils. A stimulating action of boron on the nitrifying bacteria seems to follow in certain cases.

The results at Orlando, where the same amounts of boron were added to the soil as at other points, but where the toxic action of the boron was marked and where soluble boron was found in the soils after several months, indicates that many factors are involved in the absorption of boron and its effect on plants, and that definite conclusions in studies of this nature should be drawn with great care. These results are submitted as a preliminary study of this question. It is our purpose to test the cumulative action of boron in soils.

Summary.

1. It apparently made little difference in the quantity of boron absorbed by the plants tested whether boron was added to the soil as borax or as calcined colemanite. The addition of lime with borax had no definite effect in preventing the absorption of boron. Wheat and oats absorbed very little boron, while leguminous and succulent plants absorbed comparatively large amounts.

2. Wheat, beets, cowpeas, and tomatoes grown in pots in the greenhouses contained boron principally in the tops of the plants, and, with the exception of the beets, comparatively little or none in the roots.

3. The fruit of the tomato plants contained only traces of boron, while the fruit of the cowpea contained large quantities. Lettuce grown in the greenhouse absorbed boron in proportion to the amounts present in the soil.

4. Potatoes grown in the open showed, when mature, a small amount of boron in the tops, and relatively large amounts in the roots and tubers.

5. The leguminous plants, string beans, soybeans, and cowpeas, which were very sensitive to boron, showed when grown in plot tests a more equal distribution of the boron among the roots, tops, and fruit than the other plants tested.

6. Radishes grown in plots contained much larger quantities of boron in the tops than in the roots. Analyses of entire plants of wheat, corn, peas, and oats grown on plots in the south showed the absorption of boron in all cases, the peas absorbing the most. All of the control plants contained at least a trace of boron.

7. Samples of soil from some of the control plots showed the presence of acid soluble boron, while several similar samples of soil from certain boron treated plots showed no acid soluble boron. Usually more soluble boron was found in the treated soil than in the control soil.

8. The yield of wheat from a plot heavily treated with borax was 90 per cent of the manured control yield and greater than the yield from the unmanured control. The wheat grains were sound and contained but a trace of boron.

9. The yield of tomatoes in pot tests were unaffected when borax was added in amounts to produce 0·0018 per cent of boron in the soil, but when the amount was increased to 0·0030 per cent a reduced yield resulted.

10. Numerous factors influenced the absorption, distribution, and action of boron in plants.

11. No more than 0·62 pound of borax or 0·75 pound of calcined colemanite should be added to each 10 cubic feet of manure, and when using the boron treated manure in growing leguminous plants, the manure should be mixed with untreated manure before being applied to the soil. For other plants, boron treated manure should not be used at a higher rate than 15 tons per acre.

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RESEARCH AS A NATIONAL DUTY.*

By WILLIS RODNEY WHITNEY.

The object of this paper is to emphasise the importance of material research and to lay stress on its necessity to any people who are ever to become a leading nation or a world power.

I have called it material research because I wanted to exclude immaterial research. I class under this head pure thought as distinct from thought mixed with matter. It is worth while making this distinction because it is not always recognised. It is very natural for us to feel we can think new things into being. Chemistry has advanced only in proportion to the handling of chemical substances by someone. When the study of our science was largely mental speculation, and the products and reagents largely immaterial, like fire and phlogiston, we advanced but slowly. Ages of immaterial research for the philosopher's stone led only to disappointment. Successful results in modern times came from *following* nature, learning by asking and experimenting, reasoning just enough from one stage of acquired knowledge to ask the next question of materials. Prof. Trowbridge, of Harvard, once said:—

"Before Galvani's time men were lost in philosophical speculations in regard to subtile fluids; *after* his experiments their thoughts were directed to the conditions of matter *immediately* about them. Benjamin Franklin brought electricity down to earth from the clouds, while Galvani's experiments brought men's minds down from the heights where they were lost, having no tangible transformations to study."

We are now being shown by systems of national development how important is the study of the properties of matter. There is no need to raise the questions of the war, nor of the relative originality of different races, nor to compare the gifts to scientific knowledge of the various world powers. We shall go only so far as to point out that in national processes there is a certain peculiar and useful attitude towards exact and new knowledge. I want to convince you if I can that in the uses of science we ourselves have much to learn and in the matter of research we are still children.

In speaking of research I do not mean to confine my thoughts to the chemists and their knowledge and literature, but rather to that science which is back of chemistry. We may call it natural science if we are careful. It includes for my present purposes all philosophy based on measurable facts. Psychology and therapeutics come under this head; so do electricity and medicine, anatomy and physics, chemistry and biology. These are inquisitive sciences, where the answers come from asking questions of nature. If I can leave with you even a faint impression of the importance of *new* knowledge, the strength to be gained from its acquirement, and the pleasure in the process itself I shall feel repaid.

As distinct from your Illinois attitude, research is *sometimes* looked upon as a remote, postponable, and especially exacting undertaking, well suited for martyrs of science and unreasoning optimists, and not at all for teachers. The historical methods of teaching have still lingering in them some of these signs. Even in our day it is sometimes said that a teacher should not be an investigator. It will take a long time to efface that idea completely, but it will be as surely forgotten as the fact that most of our older colleges were once religious centres. It is important to realise that the need, facilities, and *possibilities* of research are all about us, retarded only by the inertia that is in us.

Every chemist, even in his freshman days, handles the identical substances with which all material advances will be made. Because he cannot always handle them in the ways of the advanced industry he is led to imagine that research is closed to him. Yet so much useful pioneer work in all fields has been done with simple material equipment coupled with good mental equipment that it almost seems as though this was the rule. The telegraph and telephone started with a few little pieces of wire wound by hand with paper insulation. The basic work on heredity was carried out by an Austrian monk with a few garden peas. The steam-engine came from the kitchen fire and wireless from the tricks of a little spark gap. There was, however, the same general kind of mind behind each one of these discoveries—the mind of the inquisitive thinker.

Advanced Training Necessary for Scientific Service.

Exactly the opposite belief is also quite common—that great advances are made by sudden flashes of thought through the mind of some lucky and presumably *unoccupied* individual. If this were so there would be little need for the high degree of training which is necessary for almost any scientific service in our day. We may find a simple illustration of this point in organic chemistry. We know that the artificial production of important chemical compounds, such as indigo and rubber, has been accomplished, but how many of us realise the training that was necessary and the research that had to be done before success could be claimed. The Badische Company spent seventeen years completing the indigo work after the *first* synthesis and expended about five million dollars before a pound was put on the market. I might say that without at least fifty years of work by thousands of research chemists neither problem could have been solved.

In my study I have a photograph of about thirty young research men grouped about Wöhler. This is the chemist of Göttingen who first discovered that an organic compound could be produced in a laboratory. It was he also who made the first metallic aluminium. The picture was taken in 1856, about as early as decent photographs were possible. Every year since 1856 that Göttingen laboratory among others has been training chemists in research. They have gone into fields of infinite chemical variety. Each man has been a centre in some distant place, and around this centre there has often been built some kind of growing chemical structure. Many became teachers, and their students in turn became experimenters and teachers. Many followed industrial chemistry and extended the field of the ever-increasing army of chemists. In my particular photograph is one man who in 1866 became the Professor Goessman of the Rensselaer Polytechnic Institute and was later Professor at Amherst and very prominent for years in the Massachusetts State Board of Agriculture.

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* From the *Journal of Industrial and Engineering Chemistry*, viii., No. 6.

Since 1856 the same seeking for knowledge by renewed groups of such men has been continually going on in many foreign laboratories. It is only slowly being taken up in the United States. Is it not time that we awakened to the fact that as research chemists we are still in our infancy? If we are ever to be a leading country in industrial chemistry research is absolutely necessary. If such research is done elsewhere then the major part of the advantage will lie elsewhere also.

Scientific research, or research in the natural sciences and in the industries, might be defined as the pioneer work of the *developed* country. In this light it is easy to see that our turn has come. Not long ago our pioneer work was of another kind; it was opening up the undeveloped land. It was actively and well done. But the work must change because our requirements have altered.

Carl Helffereich, Director of the Deutsche Bank and Secretary of the Treasury of Germany, writing before the war said:—

"All economic labour aims at making external nature contribute to the needs of man. It is as true of the primitive gathering of roots and berries as of the production of cyanamide or calcium nitrate. The enormous progress of modern economic technique is due to the splendid development of the natural sciences and the systematic application of scientific knowledge to economic labour. Physics, chemistry, and electricity have outvied each other in their influence upon economic technique."

Speaking of the scientists he says:—

"Our hermit poets and thinkers converted themselves more and more during the past century into practical creative workers, and an enormous expansion of activity has resulted from the progress of the pure and applied natural sciences."

American chemists have had German chemists pointed to as examples almost long enough, but there is some value in concrete examples, and I cannot refrain from comparing our own impoverished condition in the matter of fixed nitrogen to that of Germany.

Excepting one or two minor attempts we Americans have made almost no study of the fixation of atmospheric nitrogen. I want you to realise the varied and expensive researches, mostly carried on abroad, which were required to reach the present position of the nitrogen question. There were in Germany, and by German capital in Scandinavia, several direct oxidation processes, carried through the experimental to the practical commercial stage. The Schoenherr process is one of these, the Birkeland and Eyde process another. The direct combination of nitrogen and hydrogen to form ammonia has been successfully developed in the German Haber process, and the cyanamide process, with all its products from carbide to ammonium nitrate, was developed in Germany. There they used not only the peculiar reactions of calcium carbide with nitrogen, but the production of the nitrogen from liquid air, the reaction between water and cyanamide to form ammonia, and then an oxidation process for obtaining the nitric acid. The oxidation of ammonia to nitric acid by such methods as the Ostwald process has been studied by many investigators since 1830, and several different schemes are now in use abroad.

At the time most of this research work was under way it was not at all clear what use was to be made of it. Much of it was *purely academic* research, but it was clear that without the knowledge itself certainly no use at all would be made of it.

I do not want you to look at research as an old, established utility. I want you to see it as I do: a powerful factor proved by the advance of the industrial welfare of the foremost countries, and a world experiment of less than a century's trial, but something still unappreciated in America. It is true that the earliest man and many of the lower animals accomplished ends by research, but I refer now to research in the natural sciences and to the research which in our day is necessary to our desired activities. These sciences are already very highly developed, and advanced education is demanded by them. For example, if I wish to cure physical ills I cannot expect to do it by reciting ancient incantations, nor by using roots and herbs, as was once customary. I must first familiarise myself with an accumulation of previous experience. I must study anatomy, physiology, chemistry, bacteriology, &c. This is a relatively recent world-condition. Conditions are similar in all the applied sciences. The accumulated knowledge in any field is already very considerable, and to get into the firing-line of useful work one must go up past the baggage-train of knowledge and experience. There is something in the blood which makes an American naturally hate preliminaries. It will be a great day when we see how important preliminaries are. The hospital surgeon well knows how much more willing the young interne is to actually handle cases, if it is only to administer the ether or the iodine, which any nurse can do, than he is to study the theory of ether as an anæsthetic, or of iodine as an antiseptic, which perhaps no nurse could understand. The young student of mechanics thinks he could have devised the steam turbine if it had not been done before his day, but when he comes to study the problem as it has actually been developed he finds the same old kinetic theories, differentials, and integrations which he spurned as too theoretical when he sought a short road to engineering.

American Progress Proportional to Preparation by Research.

I want you to realise that in America we are going ahead in the future at a rate dependent *entirely* upon our preparation. Laboratories are a relatively modern thing. In most of the sciences they are a development within the lives of men now living. I want you to see that we must be foremost in systematic, organised research, or we shall be distanced by other countries which already well recognise the value of *new* knowledge.

When so much of our material welfare, the condition and extent of our manufactures, the quality of our agricultural efforts, and the health of our people depend upon the rate of our acquirement of *new* knowledge there ought to be much greater effort made along the lines of research than is at present the case. We call knowledge power, but we need to see that *new knowledge* is the second power of power.

I would rather be a little Moses than a big Jeremiah. I would much rather point a way to a promised land, however remote, than talk about our lamentable conditions. But we Americans are not sufficiently imbued with the spirit of active and efficient service. We are a preliminary experiment on the possibility of operating a competitive nation in a democratic manner, but we don't care enough about it. We have about as little interest in the wonder and elasticity of nature, the laws of materials (except where they affect our stomachs and our health), as had Darwin's starving Patagonians. With us the spirit of the hive is confined to the bees. Germans and Japanese make better scholars than we do, and a Chinese laundryman sticks longer to his daily job and talks less about it. We are living in the Garden of the Gods, but we are still eating grass.

Is there no significance in the fact that many American colleges are better known through their foot work than their head work? Is it not significant that the Y.M.C.A.'s dotting our land are as strong in bowling alleys as in education, and that most of our religious training goes to the heathen? Is it a sign of health that so large a portion of our newspapers are paid to feed us with results of useless experiments between prizefighters? I think the stadium should be the accessory of the laboratory, not the temple of the oracle, and that in reality a research laboratory is more compatible with the object of a university than is the more common training table. I do not mean to be too insistent as a critic or too pressing as an advocate, but I hate to see my own country such a trailer as it now is. I hope the conditions are changing, but I know they are not changing fast enough. Probably Moses and Jeremiah were both right.

All service is based on knowledge, and knowledge is an ever-augmenting thing which almost anyone may increase. If the stock is *eternally* useful, as it is, how great must be the value of the *indestructible* increments which *anyone* may produce. I do not think due reverence is given to new knowledge. I want to illustrate.

(To be continued).

ON THE OCCURRENCE OF PYRITIC NODULES WITH NUCLEI OF CARBON.

We have received the following interesting communication from a correspondent:—

There occurs in the oasis of Khargeh in Egypt, adjacent to the offices of the Corporation of Western Egypt (now in liquidation), an outcrop of sandstone rock, containing nodules of varying size, mostly iron pyrites (these are quite distinct in appearance from botryoidal pyrites). They lie on the ground as rounded blackish lumps with roughened surfaces; they contain in many, if not in all, cases nuclei of carbon resembling graphite, anthracite, or charcoal. In one specimen that was for some years kept under a glass case in the office at Cairo the carbon centre was as large as a pigeon's egg; after a couple of years a white and yellow efflorescence appeared on the fractured surface.

The special interest in this matter seems to lie in the following:—

For many years the Arabs of the Western Desert have declared that diamonds are obtained from the nodules that lie exposed in a certain region of the Farafra Desert, exposed of course by the weathering of the rock.

Now in most parts of the Western Desert the rock is limestone and the nodules are siliceous. They lie sometimes in long lines three or four deep for many hundred yards, and are occasionally as large as 10 to 15 inches in diameter. I have broken many, but have never found any carbonaceous matter.

Still, there is no doubt whatever that the Bedouins crossing this particular region (Farafra) invariably search for and bring in nodules, if they can hear anything rattling inside. I know a well authenticated case where a coastguard official (English), whose men captured a Bedouin caravan with smuggled salt, found several of these nodules in the sacks; these were taken by his men, and one assured him afterwards that a goldsmith in Assiout had given him £6 for the stone inside. Of course an Eastern goldsmith might mistake a bright quartz crystal for something valuable.

However, the road from Dakhla to Farafra crosses the Nubian sandstone. Nodules in this region (which I have never visited) are probably not siliceous nodules at all, but pyritic, and this occurrence of carbon nuclei in the Khargeh nodules suggested that there may be carbon nuclei in the Farafra nodules.

Again, the Western Desert has been the scene in comparatively recent geological periods of violent volcanic action. I have seen between the region of Cairo and Assiout four large areas of basalt-outflows; in one case, west of Deirout, the entire surface of the limestone desert rises in a dome about five miles across, in the middle of which is a black basalt hill about 80 feet high and 200 feet wide at the base. Apparently this never got through the upper beds which have since been degraded around it.

The fault responsible for the Khargeh oasis is, I think, a clear drop of some 300 feet; in any case the movement since the sandstones were laid down have been very extensive and the pressures very great.

The point I should like to submit to your judgment is this: Given carbon nuclei of considerable size in the large pyritic nodules, in beds subjected to sudden vast pressures, is there any possibility of the crystallisation of the carbon? The pyrites would, I suppose, be greatly altered at the time. Unfortunately I have never seen one of these nodules said to contain diamond.

I may add that I have had large nodules brought in to me from Sinai Desert that had evidently once been pyritic, but were now mostly sulphur and iron oxide.

NOTICES OF BOOKS.

A Study of the Preparation of Frozen and Dried Eggs in the Producing Section. By M. E. Pennington, M. K. Jenkins, and W. A. Stocking, assisted by S. H. Ross, E. Q. St. John, Norman Hendrickson, and W. B. Hicks. Washington: Government Printing Office. 1916. Pp. 99. Price 30 cents.

In this bulletin the information which was collected during the investigation of the preparation of dried and frozen eggs, begun in 1912, is given in full. The subject was attacked both from the practical and purely scientific sides, and the Department of Agriculture had to do pioneering work to put the new industry upon a scientific basis. The investigation appears to have been entrusted to very capable hands, and the results obtained will be of great value both to those who are managing egg-breaking plants and to chemists and bacteriologists engaged in food investigation. Among other suggestions it is recommended that very great stress should be laid upon careful grading and bacteriological cleanliness, and that only two grades of canned eggs should be prepared, food eggs and tanners' eggs.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 20, May 15, 1916.

Catalysis of Hydrogen Peroxide in a Heterogeneous Medium. Part IV. Experiments with Carbon. Conclusions.—Georges Lemoine.—As before the catalysis experiments were carried out in a glass tube, using Merck's hydrogen peroxide purified by distillation. Coconut charcoal, wood charcoal, and sugar charcoal were used in turn, and the influence of the weight of the catalysts and the velocity of reaction were determined. It was found that all three varieties of carbon act as catalysts, coconut charcoal being the most energetic. The catalytic effect seems to be related to the power of absorption of gases, and in many ways charcoal resembles platinum in its action. Many important conclusions may be drawn from the author's work on catalysis. Thus he finds a lowering of temperature for the same velocity of decomposition of H_2O_2, which would decompose of itself but only very slowly. The rate of decomposition increases with the weight of the catalyst, but not proportionally; it also increases with the state of division; that is to say, with the active surface of the catalyst. The action only extends to a very small distance through the liquid. The catalysts studied can be divided into two distinct groups; firstly, chemical catalysts, with which the action is due to the formation of a temporary unstable compound. Experiments with mercury show clearly the temporary formation of an oxide. The experiments with oxides may be interpreted by the formation of unstable peroxides, destroyed at a certain moment, but much more quickly than mercury oxide. Experiments with platinum black can be explained only on the supposition of the formation of a particular compound, for in the same state of division platinum black is much more energetic than spongy platinum. The second group comprises physical catalysts, such as the several varieties of carbon and spongy platinum, and in this group the action appears to be connected with the power of condensing gases. Catalysts can function as both chemical and physical agents; as, for example, the very finely divided oxides and platinum black.

Determination of Carbon by Eggertz Method.—H. Le Chatelier and F. Bogitch.—Variations in the rate of cooling very considerably modify the coloration due to carbon, and the influence of the rate is more marked the richer the metal is in manganese. The coloration may be reduced by a third; that is to say, if the carbon is determined colorimetrically in a rapidly cooled steel by comparison with a specimen of the same composition cooled slowly the determination may give a result a third too low. The authors' experiments show that if the Eggertz method is used to determine carbon it is indispensable that the specimens of steel should be cooled slowly, and that the metal used for comparison should contain the same percentage of manganese as the steel studied.

Formation of Pyridic Bases from Albumenoids.—L. C. Maillard.—In a recent note A. Pictet and Tsan Quo Chou (*Comptes Rendus*, 1916, clxii., 127; Chemical News, 1916, cxiii., 108) have described the formation of pyridic and isoquinoleic bases by condensation of nascent formic aldehyde with the products of acid hydrolysis of casein. This result confirms the author's conclusions reached many years ago. He showed that amino acids (products of the hydrolysis of albumenoids) condense very readily with the aldehyde function of sugars, and that the products of condensation (humic matters) give large quantities of pyridic bases when exposed to pyrogenation. Thus the above authors have only replaced the aldehyde alcohols of M. Maillard by simple methanal, and the individual amino acids by the products of hydrolysis.

Diphenylpyruvic Acid.—R. Hemmerlé.—Although free crystalline phenylpyruvic acid is represented by the enol formula $C_6H_5—CH=COH—CO_2H$ it is very readily transformed into α-cetonic acid, and often reacts in this form. The author has investigated whether most α-cetonic acids can combine with themselves by aldolisation to give a diphenylpyruvic acid, and finds that this is the case. The condensation can be effected by starting with the acid itself and using dilute soda, but the yields are poor, and a better result is obtained by using the methyl and ethyl ethers of phenylpyruvic acid which, when condensed by aqueous soda, ammonia, or even potassium bicarbonate, give good yields of diphenylpyruvic acid.

Phenyloxymaleic Anhydride.—J. Bougault.—Phenyloxymaleic anhydride is obtained by the action of sulphuric acid upon the ether of α-cyano phenylpyruvic acid. In order to isolate the unstable anhydride it is necessary to take special precautions and keep the temperature low. The same substance can be prepared by dissolving the ether of phenyloxalacetic acid in sulphuric acid and allowing to crystallise. The anhydride crystallises with one molecule of water, and thus possesses the same composition as phenyloxalacetic acid, but is readily distinguished from it by its reactions with alcohols and amines. When hydrated it fuses below 100°, but if it is dried at a low temperature a compound is obtained which fuses at 163°. The hydrated substance easily dissolves in warm benzene, while when anhydrous it hardly dissolves at all. In both states it is insoluble in water, very soluble in alcohol, acetone, and ether. It decomposes in presence of water, slowly in the cold, and rapidly on heating, giving carbon dioxide and phenylpyruvic acid. When heated to 100° with an alcohol it gives the ether of phenylpyruvic acid and carbon dioxide. With amines molecular compounds are first formed, then carbon dioxide is evolved, and with primary and secondary amines a substituted amide of phenylpyruvic acid is formed. With tertiary amines a salt of phenylpyruvic acid is obtained. Ammonia acts on the anhydride instantaneously in the cold, giving the amide of phenylpyruvic acid.

MISCELLANEOUS.

Liebig's Extract of Meat Company, Limited.—At a board meeting on July 13 it was resolved that, subject to confirmation at the 51st Ordinary General Meeting of the Company to be held on August 2, an additional dividend of 10 per cent and a bonus of 5s. per share, both free of income tax, on the ordinary shares for the year ended March 31, 1916, shall be payable on and after August 3 to proprietors who are registered on the Company's books on July 22, and to holders of ordinary share warrants to bearer. This dividend and bonus, together with the interim dividend paid on February 22 last, amounts to 25 per cent, free of income tax, for the year.

Association of British Chemical Manufacturers.—The support that has been accorded to this Association during the short time the movement has been on foot, affords convincing evidence that British chemical manufacturers are fully alive to the necessity for organisation and co-operation in the widest sense. A number of the leading manufacturers have already signified their intention to become members of the Association, and every day brings fresh adhesions. Some doubt having been expressed that the Association might become too capitalistic in nature, especially when it became known that the subscription was to be based on the capital of the member firms, it may be stated that each firm joining the Association will have only one vote in its affairs, irrespective of the amount of subscription paid. Provided that adequate support from British manufacturers is forthcoming, the Association will undoubtedly prove to be of the greatest assistance and benefit to the chemical industries of the country. The affairs of the Association are in the hands of a provisional committee, consisting of Dr. E. F. Armstrong (Joseph Crosfield and Sons), Mr. F. W. Brock (Brunner, Mond, and Co.), Dr. Charles Carpenter (South Metropolitan Gas Company), Dr. M. O. Forster, F.R.S. (British Dyes), Mr. John Gray (Lever Brothers), Mr. C. A. Hill (British Drug Houses), Mr. Norman Holden (Hardman and Holden), Mr. C. P. Merriam (British Xylonite Company), Sir Alfred Mond, Bart., M.P. (Mond Nickel Company), Mr. Max Muspratt (United Alkali Company), Sir William Pearce, M.P. (Spencer, Chapman, and Messel), Mr. R. G. Perry (Chance and Hunt), Mr. R. D. Pullar (Pullars' Dye Works), Dr. Alfred Ree (Society of Dyers and Colourists), Mr. A. T. Smith (Castner-Kellner Alkali Company), and the Right Hon. J. W. Wilson, M.P. (Albright and Wilson). This Committee has prepared draft constitution and rules of the Association, copies of which can be obtained from the Acting Secretary, Mr. T. F. Burton, Broadway Chambers, Westminster, S.W.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Glycerin Substitutes.—We shall be much obliged if any reader can favour us with the names and addresses of manufacturers or suppliers of glycerin substitutes.—Pioneer Health Food Co.

The Weed called "Couch."—(Reply to H. M. Gledstone).—This is the rhizome or underground stem of *Triticum repens*, or couch grass. Used in the form of decoction, it has undoubted value in bladder troubles. Mr. Gledstone should write Mr. E. M. Holmes, Pharmaceutical Society, 17, Bloomsbury Square, London, W.C., who will give complete information.—Frank Browne, 60, Fornham Road, Bury St. Edmunds.

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SUGGESTION CONCERNING THE STATEMENT OF THE PHASE RULE.

By THEODORE W. RICHARDS.

The most serious difficulty of the Phase Rule for beginners lies in the definition of the word "component," of which many varying definitions have been given by various authorities. Of these most are entirely legitimate, although they may lead to different choices as to the number of components in special cases (see, for example, "The Phase Rule," by Alex. Findlay, London, 1904, p. 12). The difficulty lies in the fact that the restrictions imposed often cause the number of "components" to be different from the number of individual chemical substances taking part in the reaction.

No attempt will be made here to give all the varying definitions or explain the limitations which must be imposed upon them. The object of this note is to advocate briefly a different method of treatment, perhaps more generally acceptable to chemists and more easily comprehensible by beginners than most of the others. Doubtless it has been used before, but it does not seem to have been clearly stated or commonly recognised. The idea is this: Instead of stating the Phase Rule in a very simple equation and placing all the burden of incomprehensibility upon the component, this method abandons the complex older idea of the component and substitutes another, that of the chemical "individual" or "constituent," which is easily understood by the chemist, and places all the necessary restrictions in definite form in a somewhat more complex but easily comprehensible equation defining the Phase Rule.

Note.—Except for the fact that in most minds conversant with the subject the term "component" indissolubly involves restrictions it would be better to retain this old term, giving it the new and simpler meaning. Prof. Lash Miller convinced me that on this account the change of meaning is undesirable. The word "individual," however (suggested in conversation by Prof. A. B. Lamb), seems to answer the requirement. The word "constituent" would be almost as good, but not quite so definite and distinctive. This, then, might be used; indeed it has already been used in a sense not very different from the present by Trevor (*Journ. Phys. Chem.*, 1896, i., 22), but his use of the word was somewhat freer than that needed here, as was also Bancroft's ("The Phase Rule," 1897, 227). The qualification given above, "undecomposed in the reactions concerned," is a very important one for the present purpose, although it does not appear in the earlier definitions. According to Bancroft's application n_r would sometimes be a minus quantity (p. 230 "The Phase Rule," a suggestive book which did much to promote study of the subject). The interesting very recent treatment of Washburn ("Principles of Physical Chemistry," N.Y., 1915) is yet different, involving another idea called the "composition number," although of course the fundamental idea is the same, as indeed it must be in any sound treatment of the Phase Rule. This present method of statement adopted above makes no attempt to define the kinetic mechanism needful for achieving the result. It records simply the facts, and may be made subject to any interpretation applicable according to any other formulation which likewise expresses the facts. Reference may be made to the interesting papers of Wegscheider (*Zeit. Phys. Chem.*, 1903, xliii., 89; 1903, xlv., 496; 1904, l., 357; 1905, lii., 171).

According to this plan the definition of the chemical "individual" is as follows:—*The* INDIVIDUALS *of any reacting system are the separate chemical substances,* UNDECOMPOSED IN THE REACTIONS CONCERNED, *which are necessary to construct the system. The number of such individuals to be chosen is the smallest number necessary to construct the system.*

If we define the individuals in this simple and reasonable way the Phase Rule may be expressed as follows, without any need of reference to the number of "components as usually defined:—

$$F = (n_i + n_E) - (n_\phi + n_r) \quad . \quad . \quad . \quad . \quad . \quad 1$$

in which F = the actual variance, or the number of degrees of freedom in the special case; n_i the number of individuals as defined above; n_E the number of physical manifestations of energy (mechanical, thermal, electrical, &c.) which are brought into play in the reaction; n_ϕ the number of phases; and n_r the number of independent restrictions or fixed conditions which are determined by the circumstances of the case but not included in the definition of the individuals. Each quantity is of course a small whole number. This method of statement separates sharply the characteristics (n_i and n_E) tending to *increase* the variance from those (n_ϕ and n_r) tending to *diminish* the variance, and seems to me to place the whole subject in a clearer light.

Ordinarily, where only mechanical and thermal energy come into play, $n_E = 2$. Then the equation for the Phase Rule becomes—

$$F = (n_i + 2) - (n_\phi + n_r) \quad . \quad . \quad . \quad . \quad . \quad . \quad 2$$

This is, of course, the ordinary statement of the Phase Rule, with the addition of n_r, the number of restrictions, as a last term. Equation 2 thus given is used in the subsequent exemplification.

Because all the subtlety of the Phase Rule is concentrated in the last new term, n_r, one must be especially careful in studying each case to be sure that the value of this term is properly estimated; in other words, to be sure that one has counted correctly all the independent restrictions. Moreover, each restriction (especially those concerning concentration, which apply to a variable phase) must be carefully examined in order to show that it is really not involved in another previously determined upon or in the definition of the individuals. This procedure of course involves thought, but I know of no method by which the Phase Rule can be applied properly to any but the simplest cases without thought according to any definition. One must remember, of course, that no restriction can be applied to the quantity of any *phase*; a drop of a solution in true equilibrium is as effective as a bucketful for the purposes of the Phase Rule. Thus in the case of calcium carbonate, discussed below, a limitation of the quantity of the carbon dioxide to that of the lime is not a real restriction. Adding more lime has no effect on the equilibrium.

In most cases no great difficulty arises in the interpretation of the new term n_r. So far as I can discover it may include only two different classes of restrictions; on the one hand, the intensity factor of some form of energy may be restricted or kept constant; on the other hand, one individual may (either from chemical necessity or arbitrary choice) be kept in definite weight-ratio to some other individual or at definite concentration in a variable phase. (The requirement that a given volume of gas shall contain a given weight is a valid restriction in this sense). This duality of type might be indicated if desired by substituting for n_r its equivalent $n_{r'} + n_{r''}$, in which the two modified subscripts represent the two different types. A new restriction belonging to either of these types adds one to their sum n_r. For example, if temperature and pressure are both fixed, but no other fixed requirements exist, $n_{r'} = 2$ and $n_{r''} = 0$, therefore $n_r = 2$. If neither temperature nor pressure is fixed, but one individual must always bear a definite quantitative relation to another, $n_{r'} = 0$ and $n_{r''} = 1$; therefore $n_r = 1$.

It will be noted that the usual definition of the number of "components" makes this number equal to $(n_i - n_{r''})$.

Let us interpret individual cases in the light of the Phase Rule equation given in terms of chemical individuals. For example, let us take the familiar case of the decomposition by heat of calcium carbonate. There we have the individuals $CaO + CO_2$, that is $n_i = 2$. When the two solids and gas are present in equilibrium $n_\phi = 3$, of course. If no restriction is placed on the concentration of the variable gas phase (or on the pressure or temperature of the gas) $n_r = 0$; therefore, $F = 1$, that is, the system is univariant. (Let me urge once more the use of the purely Latin terms univariant, bivariant, &c., as indicating the degrees of freedom instead of the hybrid Greek-Latin terms monovariant, &c. This consistent terminology was suggested in 1898, *Am. Journ. Sci.*, [4] 1898, vi., 201. It has been supported also by Trevor, but has not always been adopted). If either temperature or pressure is fixed $n_r = 1$ and $F = 0$.

Another familiar case is the case of steam, oxygen, and hydrogen in equilibrium at a high temperature, the hydrogen and oxygen being in equivalent proportions resulting from the decomposition of water. The usual definition of component would give only one component to this system, but many chemists may be better satisfied by taking, according to the definition given above, hydrogen and oxygen as the "individuals" concerned making $n_i = 2$. As there is only one phase, $n_\phi = 1$, and here $n_r = 1$, because a restriction is placed on the ratio of concentrations of the oxygen and hydrogen in the single phase, which is a variable one; therefore $F = 2$, and the system is bivariant.

It may be noted that the essential question of this kind of restriction is concerned with the variable phase, and involves the relative concentration of the individuals in this phase. The variable phase always holds the key to the situation.

Taking a more complicated case, we see that the definition applies equally well, for example, to a mixture of a dilute solution of sodium bromide and potassium chloride in equilibrium with its vapour. If the solution remains dilute and no new phase appears, this may be looked upon from two equally legitimate points of view. In the first place we may take as the individuals of the system sodium bromide, potassium chloride, and water—that is, $n_i = 3$, $n_\phi = 2$, $n_r = 0$; therefore $F = 3$. On the other hand, we may look upon the individuals as the four ions Na′, Br′, K′, Cl′ (or the four corresponding elements), and water—five in number, bearing in mind later the two independent restrictions: concentration Na = concentration Br, and concentration K = concentration Cl. According to this better interpretation, we should have $n_i = 5$, $n_\phi = 2$, $n_r = 2$; therefore $F = 3$ as before.

A regards the former of these interpretations, trouble begins in a case of this kind when the solution is so far evaporated that a metathetical product separates out, or when a new salt containing the same elements (*e.g.*, sodium chloride) is added. In that case, although the elements and ions present remain the same, a new individual, in the sense used in this interpretation, has really been added, and the old, usually accepted explanation is somewhat puzzling, although it is legitimate (see, for example, Bancroft, "The Phase Rule," 1897, p. 230).

On the other hand, the latter interpretation, involving five individuals, which is now demanded by the strict phraseology of the definition of the term, offers no difficulty whatever. Thus, if with this system sodium chloride separates (both the other salts being decomposed in the process, but the five individuals remaining unchanged), the two restrictions named above have merged into one. (It is true that this restriction existed in the system before the NaCl was added, but it was not independent of the other two previously present). Concentration (K + Na) = Concentration (Cl + Br), and the new freedom is exactly offset by the new phase—*i.e.*, $n_i = 5$, $n_\phi = 3$, $n_r = 1$; therefore $F = 3$. Similar reasoning is involved if a little sodium chloride is dissolved in the dilute solution of KCl and NaBr without causing the appearance of a new phase, but here, of course, the result is $F = 4$.

These considerations and others lead me to the conclusion that the use of the conception of chemical "individuals" as defined above gives greater flexibility and clearness than the usual way of first calculating components and then considering those in the Phase Rule equation.

The mathematical verification of Equations 1 and 2 follows directly, it seems to me, from that of the old familiar Phase Rule equation; they are really only different methods of stating the same idea.

Perhaps it may be worth while to give here a brief statement of an inductive method of presenting the Phase Rule, which I have found very efficacious for beginners. Doubtless others have used this method, but I do not know of its having been published, and it was independently evolved here. (Essentially the same method has been suggested but not amplified in the clear explanation of the Phase Rule in "General Principles of Chemistry," by A. A. Noyes and Sherill, 1914, p. 95). After the student has become familiar in the laboratory with such well-known phenomena as the dependence of boiling-point and freezing-point on pressure and their definiteness under constant pressure with one individual, and after he has further made himself practically acquainted with the boiling-points and freezing-points of definite solutions, and with cryohydric and transition points and kindred phenomena, his knowledge may be summed up as follows:—

With one individual a fixed point (where $F = 0$) is determined by:—

	Total fixed conditions.
The co-existence of 3 phases	3
" 2 phases and definite pressure	3
" 2 phases and definite temperature	3
" 1 phase and definite pressure and temperature	3

With two individuals (*e.g.*, H_2O and Na_2SO_4) a fixed point is determined by:—

The co-existence of 4 phases	4
" 3 phases and definite pressure	4
" 3 phases and definite temperature	4 4
" 2 phases and definite pressure and temperature	4 4
" 2 phases and definite temperature and defined concentration	4

The same method may be extended to more complicated systems and enforced with diagrams which make clear the fixity of these several points. The student thus sees that three fixed conditions are necessary for invariance with one individual, four fixed conditions with two individuals, five fixed conditions with three individuals, and so on. He sees, further, that the restricting of any of the variable conditions produces exactly the same effect as the addition of another phase. Thus he perceives that it is legitimate to add n_r to n_ϕ in the expression for the Phase Rule. Of course the number of degrees of freedom are simply the number of additional restrictions which it is necessary to add to any given system in order to attain invariance.

After the student has become thoroughly familiar with examples in which pressure and temperature are the only energetic intensity factors to be considered other manifestations of physical energy may be brought in, and the student is shown the effect of changing surface tension produced by variation in the size particles, with its consequent effect upon solubility, the question of electromotive force, &c., using Equation 1 above. (As Trevor has pointed out—*Journ. Phys. Chem.*, 1897, i., 349—the ordinary two-fluid "reversible" cell is not in true equilibrium because of the osmotic pressure and diffusion at the junction of the two liquids. The beginner is therefore advised not to attempt the application of the Phase Rule to such cases, which are full of pitfalls. A much simpler case is a dilute amalgam cell with two concentrations of amalgam as the two electrodes. Here the concentration of the electrolyte is without influence and does not form another restriction—Richards and Lewis, *Zeit. Phys. Chem.*, 1899, xxviii., 7).

This outline is of course merely a sketch of the method. It needs amplification with the help of many examples, which can easily be provided by anyone even moderately familiar with the principles evolved.

Summary.

To sum up briefly the contents of this note: The idea of the component is replaced by that of the "individual," which is defined in the simplest possible way as an undecomposed chemical substance necessary for constructing the system under consideration, and the number of individuals needed to satisfy the Phase Rule is taken as the least number of such "individuals" needed to construct the system. Into the equation representing the Phase Rule and expressing the number of degrees of freedom of the system is then introduced a term giving the maximum number of independent restrictions involved in the fixation either (*a*) of one or more of the intensity-factors of the forms of physical energy concerned, or (*b*) of some concentration-relation of the individuals in the variable phase. A somewhat obvious method of evolving the Phase Rule inductively for beginners is sketched.

This note is intended rather as the suggestion of an idea than as a final or complete statement of the case. The nomenclature is subject to change if better designations can be found. The object of the note is to remove if possible the most serious stumbling-block from the path of the beginner.—*Journal of the American Chemical Society*, xxxviii., No. 5.

TITRATION OF NITRATES WITH FERROUS SULPHATE.

By FRED C. BOWMAN and W. W. SCOTT.

The great variety of methods of determining nitrates found in chemical literature shows the need felt by chemists for simpler ways of making this important analysis. Most methods now in use involve distillation or evaporation, or the use of special apparatus, all of which take a good deal of time and attention.

The method proposed by the authors is as easy and quick as any ordinary titration, has a wide range of usefulness, and is accurate enough for most purposes.

Bibliography.

The first mention of the method was made by Grossart in 1847 ("Sur un Nouveau dosage de l'Acide Azotique et des Azotates," *Comptes Rendus*, 1847, i., 21). He titrated nitrates in boiling 60 per cent sulphuric acid with a ferrous sulphate solution, using ferricyanide as an outside indicator. He gives no details or test analyses. No doubt his results were less accurate than he thought.

Mohr announced the discovery of the method in 1861 (*Dingler's Polytech. Journ.*, 1861, clx., 219). He dissolved the sample in sulphuric acid (diluted 1 to 9), and titrated at 70° to 80° C. with a ferrous sulphate solution containing 200 grms. of the salt per litre, using as the end-point the appearance of a brownish colour. He declared that it was a good technical method, but Fresenius (*Zeit. Anal. Chem.*, 1862, i., 32) and Eder (*Ibid.*, 1877, xvi., 267), who examined it later, condemned it strongly.

In 1899 van Deventer carried out the reaction over mercury in a Crum tube with exclusion of air, using fairly strong sulphuric acid as a medium and a weak ferrous sulphate solution as reagent (*Zeit. Phys. Chem.*, 1899, xxxi., 50). The process was awkward to handle.

No comment on these methods was found in the journals, and evidently they failed of acceptance. They were all based on the reduction of the nitrate to NO and not to N_2O_3, as in the method given below, for estimations in presence of sulphuric acid. No mention of acids other than sulphuric was found in the literature.

Estimation of Nitric Acid in presence of Arsenic Acid.

The writers devised the method given below originally for the purpose of estimating nitric acid in arsenic acid. The original form of the method was as follows:—

Dilute the sample to be tested to 100 cc. with nitre free arsenic acid of such strength that there is not more than 20 per cent water in the mixture. Then titrate with a ferrous sulphate solution containing 264·7 grms. $FeSO_4.7H_2O$ and 50 cc. strong sulphuric acid per litre (1 cc. = 0·02 grm. HNO_3). Standardise the solution on a known amount of nitric acid. The following reaction occurs:—

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + 4H_2O.$$

The ferrous sulphate forms a dark brown colour, which disappears on stirring as long as any nitric acid remains. The end-point is the first permanent brown, and is readable to 0·03 cc. During the first two-thirds of the titration the ferrous sulphate is taken up very quickly; then a lively evolution of NO commences, and continues to the end. It would be thought that the oxygen of the air might re-oxidise the NO and cause error in the titration, but this does not occur.

The presence of too much water in the solution makes the reaction "hang"; *i.e.*, refuse to begin. If the solution is warmed with a few cc. of the ferrous sulphate solution the reaction begins abruptly, and runs easily thereafter. Heating even to boiling does not change the reaction, but may volatilise some of the HNO_3. There should not be more than 25 per cent of water present at the end of the titration. Water added in the ferrous sulphate solution must be taken into account.

In the light of subsequent knowledge it would seem better to make up the standard solution without any sulphuric acid. The proportion of sulphuric acid present in a titration was, however, so small that its influence could not be detected.

A few analyses will show the accuracy of the method.

Per cent HNO_3 *in Arsenic Acid.*

Nitrometer	0·25
Ferrous sulphate method	0·27

Nitric acid was added to nitre-free arsenic acid and the mixture analysed:—

	1.	2.	3.
Grms. nitric acid taken ..	0·6610	0·5968	0·0661
Grms. nitric acid found ..	0·6608	0·5984	0·0660

A small excess of ferrous sulphate is necessary to give a good colour at the end-point. Usually, this does not amount to more than 0·1 cc., but for small quantities of nitrates the correction is greater. In this case a little nitric acid should first be added to the arsenic acid, and titrated with ferrous sulphate to a brown tint; then the sample to be tested may be added and titrated accurately.

Estimation of Nitric Acid in presence of Phosphoric Acid.

The same reaction between ferrous salts and nitrates occurs in phosphoric as in arsenic acid, but titrations are even more satisfactory. No heating is required to start the action, and the end-point is a little sharper than in arsenic acid, being readable to about 0·02 cc. with the ferrous sulphate solution described above. Practically no excess is required at the end-point, except for very small amounts of nitrate. As with arsenic acid, the concentration of water present at the end of a titration should be less than 25 per cent, and better results will be obtained with 20 per cent.

Below are a few test analyses made in phosphoric acid:

	1.	2.	3.
Grms. HNO_3 taken ..	0·6610	0·5968	0·5968
Grms. HNO_3 found ..	0·6618	0·5984	0·5966

Estimation of Nitric Acid in presence of Sulphuric Acid.

Both arsenic and phosphoric acids have the drawback that they are too expensive for general use in titrations. Sulphuric acid is the only strong acid available in the laboratory at a reasonable price. When this was tried the surprising fact was discovered that the reaction proceeds only two-thirds as far as in arsenic and phosphoric acids. Nitrates are reduced, not to NO, but to N_2O_3. Strong heating will, however, drive the reaction somewhat further. The reaction that occurs in the cold is therefore:

$$4FeSO_4 + 2HNO_3 + 2H_2SO_4 = N_2O_3 + 2Fe_2(SO_4)_3 + 3H_2O.$$

The end-point is a delicate pinkish brown, not so sharp as with the other acids, but as easy to read as the usual methyl-orange end-point in acid titrations.

Effect of Water.—Experiments showed that water slows down the reaction and weakens the colour of the end-point, so that a considerable excess of ferrous sulphate is required to give a readable tint. Larger quantities of water stop the reaction entirely in the cold.

Per cent water at end-point.	Grm. HNO_3 taken.	Grm. HNO_3 found.
15	0·4963	0·4935
20	0·4963	0·4923
20	0·4963	0·5024
25	0·4963	0·4973
35	0·5968	0·6808

These figures are not of high accuracy, but they show that 25 per cent of water is permissible as a maximum, though it makes a rather difficult end-point.

Effect of Temperature.—The temperature of titration should be low. Too high a temperature acts in two opposite ways:—(1) It causes volatilisation of HNO_3, which leads to low results; (2) it causes a slight reduction of N_2O_3 to NO, which makes for high values.

Maximum temperature during titration (°C.).	Grm. HNO_3 taken.	Grm. HNO_3 found.
40	0·4963	0·4960
50	0·4963	0·4947
60	0·4963	0·4940
90	0·4963	0·5038
110	0·4963	0·5460

The lowest temperature gives the best results; at medium temperatures the compensation of errors is fair but irregular; at high temperatures the results are high and the end-point is very bad. The conclusion is that the temperature should be kept as low as possible, and should not exceed 60° C. So much heat is generated by running the ferrous sulphate solution into the sulphuric acid that the test beaker must be cooled in a bath of water during titration.

Correction for End-point.—It was found that ferrous sulphate attacks N_2O_3 slowly under the conditions of the titration, but that it has so marked a preference for HNO_3 that no reduction of N_2O_3 occurs while HNO_3 is present. As the brown colour of the end-point is due to the formation of a compound of $FeSO_4$ and NO, some slight reduction to NO must occur always. The results of many experiments show that about 0·2 cc. excess of ferrous sulphate solution (1 cc. = 0·02 grm. HNO_3) is required to give the brown tint of the end-point in a volume of 100—150 cc. This holds for titrations ranging from 0·5 cc. to at least 80 cc.

Effect of commonly occurring Impurities.—The effect of impurities ordinarily occurring in nitrates was investigated by adding them to a known amount of nitric acid and titrating the latter. Table A gives the results.

The table shows that nitrite has little effect; chloride, iodide, and bromide cause low results in quantities as little as 2 per cent, and chlorate, bromate, and iodate cause high results. Elsewhere in this paper it is shown that ammonium salts have no effect.

TABLE A.—*Influence of Salts on Ferrous Sulphate Titration for* NO_3 *in presence of Sulphuric Acid.*

(Amount of HNO_3 taken, 0·3039 grm.).

Formula.	Salts added to HNO_3. Weight. Grm.	Per cent of mixture tested.	Titration. Cc. $FeSO_4$ solution.
Blank	None	—	15·8
KNO_2	0·08511	21·9	15·71
KNO_2	0·4256	58·6	16·06
KNO_2	0·8511	73·0	16·76 (*a*)
NaCl	0·05846	16·0	14·96
NaCl	0·2923	49·0	— (*b*)
NaCl	0·00585	1·9	15·65
KI	0·166	33·2	11·4
KI	0·017	5·3	15·25
KI	0·0017	0·57	15·8
KBr	0·1190	28·0	— (*b*)
KBr	0·0119	3·8	15·66
$KClO_3$	0·3039	50·0	45 0 (*c*)
KIO_3	0·10701	26·0	17·36
KIO_3	0·01070	3·4	15·96
$KBrO_3$	0·0835	21·6	— (*b*)
$KBrO_3$	0·00835	2·7	16·06

(*a*) Odour of N_2O_3 evident.
(*b*) No distinct end-point.
(*c*) No good end-point.

Procedure Recommended.

Based on the foregoing results the following standard procedure is recommended for the analysis of nitrates with concentrated sulphuric acid as the medium.

Ferrous Sulphate Solution.—Dissolve 176·5 grms. $FeSO_4 \cdot 7H_2O$ in 400 cc. water. Stir into this gradually 500 cc. of dilute sulphuric acid, made by mixing equal volumes of water and concentrated acid. Cool the mixture, and make up to 1000 cc. The order of mixing given above should be followed, for a different order is apt to cause precipitation of an iron sulphate that cannot be re-dissolved.

1 cc. = 0·02 grm. HNO_3 and contains 0·8 cc. water.

Standardising.—Either potassium bichromate or nitric acid may serve for a standard. (Potassium nitrate may be used for standardising, but it involves more work than the use of nitric acid. To dry a sample of potassium nitrate and test it for impurities, particularly sodium, is more troublesome than to titrate a nitric acid solution. The writers met trouble in using a supposedly pure sample of potassium nitrate for standardising, and for that reason abandoned it in favour of nitric acid). With the former, estimate the strength of the iron solution by Penny's method. Remember to allow 0·2 cc. for the end-point in titrating nitrates.

$$1 \text{ grm. } K_2Cr_2O_7 = 0{\cdot}6426 \text{ grm. } HNO_3.$$

A more satisfactory method of standardising is to titrate a nitric acid solution of known strength under the exact conditions in which the iron solution is to be used. For this, dilute 41 cc. of the usual 70 per cent laboratory nitric acid to 1000 cc., and titrate with normal caustic alkali. Use 10 cc. of the dilute nitric acid to standardise the ferrous sulphate solution in the manner described above.

A certain solution standardised carefully by both methods gave the following results, showing that the methods agree well:—

1 cc. = 0·02068 grm. HNO_3 (HNO_3 as standard).
1 cc. = 0·02073 grm. HNO_3 ($K_2Cr_2O_7$ as standard).

Titration.—The sample should be chosen to contain 0·3 to 0·6 grm. HNO_3. For the most accurate work the titration should be on practically the same quantity of HNO_3 as was used in standardising the solution.

Place 100 cc. concentrated sulphuric acid, free from nitrates, in a 250 cc. beaker set in a large porcelain casserole full of cold water. Run the sample in slowly from a 10 cc. pipette to the bottom of the acid, stirring meanwhile with the pipette; this procedure is designed to prevent loss of nitric acid fumes. Run in the ferrous sulphate solution slowly in a fine stream with constant stirring until the solution turns from yellow to faint brown or pink. Then rinse out the pipette (the pipette used for measuring the sample should be graduated to contain, not to deliver) by sucking it full of the acid and draining it, and continue titrating cautiously to the first colour change. The end-point is clear to 0·05 cc.., and different operators should agree within 0·1 cc.

The casserole of water serves the double purpose of cooling the acid and making the end-point much clearer. It is sometimes necessary to halt the titration and let the solution cool. The temperature should never exceed 60° C., and is better kept below 40° C.

Let the burette stand five minutes before taking the reading as the ferrous sulphate solution drains very slowly.

Some Industrial Applications of the Method.

Nitric Acid in Oleum (Fuming Sulphuric Acid).—Weigh about 10 grms. of the oleum in a pipette and titrate according to the scheme given above. A pipette of known content may be used for routine work, so that weighing is unnecessary. This method does not estimate nitrous acid in the oleum.

The accuracy of the ferrous sulphate method was given a rigid test by two laboratories by analysing the same lot of samples independently, and afterwards comparing the results (Table B).

Table B.—*Per cent Nitric Acid in Oleum.*

	Seller's analyses. $FeSO_4$ method.	Buyer's analyses. Nitrometer method.	Difference.
I. ..	2·40	2·35	+0·05
II. ..	2·82	2·79	+0·03
III. ..	3·23	3·26	−0·03
IV. ..	3·35	3·39	−0·04
V. ..	3·52	3·57	−0·05
VI. ..	3·50	3·53	−0·03
VII. ..	3·48	3·50	−0·02
VIII. ..	3·57	3·58	−0·01
IX. ..	3·53	3·57	−0·04
X. ..	3·56	3·56	—

The ferrous sulphate method is the quickest and probably the most accurate way of determining nitrates in oleum.

Ammonium Nitrate.—A test on pure salt showed:—

Taken	0·5000 grm.
Found	0·5004 „

The method has been used extensively in one laboratory for the rapid determination of nitrates in the presence of nitrites and ammonium salts. This would be a laborious analysis by the usual methods.

Sodium and Potassium Nitrates.—Samples of chemically pure potassium nitrate and a sample of commercial nitrate of soda were tested with the following results:—

	1.	2.
Grm. KNO_3 taken	0·7000	0·3510
Grm. KNO_3 found	0·6997	0·3510
Commercial $NaNO_3$ .. By Devarda's method	97·62 per cent	
By $FeSO_4$ method ..	97·65 and 99·13 per cent	

In the latter case the end-point was bad, and the impurities present caused poor agreement between duplicates. This method is only roughly correct for impure nitrate of soda.

"*Mixed Acid*" (*Nitric and Sulphuric Acids.*)—Samples of mixed acid weighing 6 to 7 grms. were diluted to exactly 100 cc. with concentrated sulphuric acid and 10 cc. portions were titrated. The ferrous sulphate solution used was only one-half as strong as is recommended above; it was made up by diluting one volume of the standard solution with one volume of 60 per cent sulphuric acid. The temperature of titration was kept down to 70° F. by the use of an ice-bath. The acids used were most carefully analysed by the evaporation method, and the ferrous sulphate solution was standardised against a mixed acid of known analysis.

	1.	2.	3.
Per cent HNO_3 by $FeSO_4$ method ..	50·32	50·16	49·49
Per cent HNO_3 by evaporation method	50·15	50·02	49·35

These analyses represent the limit of accuracy attainable by this method. Reasonable care to observe constancy of conditions permits an accuracy of 1 in 300, where large amounts of nitrates are present.

Summary.

I.—The authors have devised a method based on the well known ferrous sulphate test for nitrates, by which large amounts of nitric acid may be titrated directly.

II.—The accuracy of the method is shown by analyses of known amounts of nitric acid combined and free, comparison being made with the usual standard methods. With care the error does not exceed 1/300 of the quantity of nitric acid estimated. The method is not suitable for traces.

III.—Constancy of conditions is important. The water content should not exceed 25 per cent of the sample titrated, and the temperature should be kept below 60° C. Chlorates, bromates, iodates, chlorides, bromides, and iodides interfere, but nitrites do not when sulphuric acid is used as a medium.

IV.—A detailed procedure for analysis is given.

V.—Some applications of the method to technical analysis are included; these are now in regular use in several technical laboratories.

In conclusion, the authors wish to acknowledge the co-operation and assistance of Mr. W. S. Allen, of the General Chemical Co., and Mr. B. S. Clark.—*Journal of Industrial and Engineering Chemistry*, vii., No. 9.

ZINGIBEROL—A NEW SESQUITERPENE ALCOHOL OCCURRING IN THE ESSENTIAL OIL OF GINGER.

By BENJAMIN T. BROOKS.

It is a well-known fact that the distilled oil of ginger, *Zingiber officinale*, Roscoe, possesses the characteristic aroma of ginger. The odour is not intense, but is very persistent, recalling sandal wood oil in this respect. Gildemeister and Hoffman state ("Die Aetherische Oele," Leipsig, 1913, ii., 292):—"Only a few of the important constituents of ginger oil are known; of the substances which give it the characteristic odour nothing is known."

In the course of an examination of ginger oil which had been freed of terpenes and sesquiterpenes, the author isolated and identified citral, methyl heptenone, nonylaldehyde, linalool, *d*-borneol, acetic and caprylic acids, combined as esters, a trace of a phenol which was probably chavicol though not positively identified, cineol, and also a sesquiterpene alcohol, $C_{15}H_{26}O$, which evidently bears the same relation to the sesquiterpene, zingiberene, as santalol does to santalene, and since it imparts to ginger oil the peculiar persistent, though mild, ginger odour, I have called it *zingeboral*. Although all of the constituents of ginger oil contribute something to the composite odour of the fresh root, the alcohol zingiberol is the only one of them possessing the peculiarly characteristic fragrance of ginger.

It should, perhaps, be pointed out that ginger oil does not produce the sharp pepper-like sensation when introduced into the mouth that is produced by the fresh root, and that the so-called "gingerol" claimed by Garnett and Greier (*Chem. Zentr.*, 1907, II., 924; 1909, II., 1593) to have been isolated by them has no existence in fact. The latter authors did not characterise their gingerol further than that it probably was a phenol and possessed a sharp stinging taste. Following their directions, I isolated from the aqueous alkaline extract, by passing in CO_2, a very small quantity, about 2 per cent. of oil, consisting of a mixture of the sesquiterpene alcohol zingiberol and a trace of a phenolic substance whose taste was phenolic and suggestive of chavicol.

Zingiberol.

From 150 grms. of ginger oil, free from terpenes and sesquiterpenes, there were obtained 41·5 grms. of oil distilling from 130° to 160° at 14 mm. pressure. By repeated fractionation, this crude fraction yielded 24 grms. of oil boiling from 154° to 157° C. at 14·5 mm. Combustion analysis gave:—

	Found. Per cent.		Calculated for	
	I.	II.	$C_{15}H_{26}O$.	$C_{15}H_{24}O$.
C	80·90	81·54	81·08	81·81
H	11·40	11·78	11·71	10·90

The substance is neither a ketone nor aldehyde. Treatment with semicarbazide in the usual manner gave negative results, and an attempt to prepare the oxime resulted in an oil entirely free from nitrogen. Nevertheless, acetylation by heating with acetic anhydride resulted in an oil containing only 17 per cent of ester calculated from the saponification number. Combustion analyses of the acetylated oil also showed that very little dehydration had taken place. Treatment of the substance with phenylisocyanate gave no phenylurethane after standing four days. This fact, together with its behaviour to acetic anhydride, indicates that the alcohol is secondary or more probably tertiary. Sodium in dry ether readily forms a sodium compound with the substance, and on gently heating with potassium acid sulphate, water is split off, yielding a hydrocarbon $C_{15}H_{24}$, boiling point 255—257°, and identical with zingiberene or *iso*-zingiberene. Combustion analysis gave:—

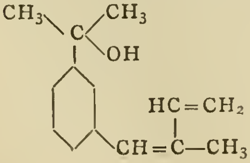
Calculated for $C_{15}H_{24}$—C, 88·15; H, 11·85. Found—88·10, 11·41.

Treatment of the hydrocarbon with HCl in glacial acetic acid yielded *iso*-zingiberene dihydrochloride m.-p. 169°.

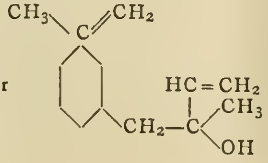
On treating the alcohol with hydrogen chloride or hydrogen bromide in glacial acetic acid solution and allowing to stand for two days, there are deposited crystals of *iso*-zingiberine dihydrochloride, melting-point 169°, or the dihydrobromide, melting point 176° (Semmler, *Ber.*, 1913, xlvi., 1822). The dihydrobromide, recrystallised from glacial acetic acid, gave the following analysis:—

Calculated for $C_{15}H_{26}Br_2$—Per cent C, 49·18; H, 7·11; Br, 43·71. Found—49·11; 7·23; 43·73.

Since zingiberol yields a dihydrochloride and a dihydrobromide identical with the dihydrochloride and dihydrobromide, respectively, of the sesquiterpene zingiberene, it is probable that on treating the alcohol with halogen acids a ring formation occurs, as has been shown by Semmler (*loc. cit.*) to be the case with zingiberene. If the constitution advanced by Semmler for zingiberene and *iso*-zingiberene are correct, then the constitution of zingiberol is probably one of the following:—



or



In working with ginger oil, the author was much impressed by the rapidity with which resinification occurs. This is particularly true of the pure hydrocarbon zingiberene, which, as Semmler has shown, contains two conjugated double bonds, as in myrcene and isoprene. The author's experience with both the distillation and extraction of fresh vetiver root, the essential oil of which also consists chiefly of sesquiterpenes and their derivatives, proved that better yields of oil were obtained and that the oil was of much superior quality when the roots were distilled or extracted within a few days of their harvest than after storage several months, as must necessarily be the case with roots shipped to Europe for distillation there. It is highly probable, therefore, that distillation or extraction of the freshly harvested ginger rhizomes would give better oil and in relatively larger yields than the dried material usually employed.—*Journal of the American Chemical Society*, xxxvii., No. 2.

RESEARCH AS A NATIONAL DUTY.*

By WILLIS RODNEY WHITNEY.

(Concluded from p. 35).

Service of Research.

SOME time, some where, centuries ago, the slag of a fireside appeared transparent; someone tried to learn more about it, and so ultimately glass was made. Research is still under way on that very material, and countless numbers of men have slowly added to the knowledge. Glass has kept the cold from the house; it has let in the light; it has renewed our eyes as they have worn out. Through telescope and microscope it has shown us the greatest and the smallest things of the universe. It has bottled our drinks and held our lights. Every year still adds new service, just in proportion as experiments add new knowledge. To-day we hear of a new glass permeable to ultraviolet light, glass opaque to X-rays, and glass for cooking utensils. Not one of these little increments will ever be lost but will continue in use, so how highly should we value them? Why did we delay so long in coming thus far, and how far or fast may we still go?

Research is preparation. It is preparing in one decade for the problems and the necessary work of the next. There are various kinds of preparedness. We are hearing a great deal about one of them nowadays,—immediate preparedness for national defence. But there is a more far-sighted preparedness that no one has adequately described and of which the building of new laboratories is a token. This type is the very best kind of preparedness for national defence if begun in time. The continued study of the secrets of nature, the uncovering of buried treasures which always seem buried just deeply enough to develop the diggers—these are the criteria of a strengthening nation.

Research presents a way, and the only certain one, of ensuring peace, of preparing successfully for defence, and of being successful in war. It is the lasting, undeviating factor which has always dominated. This may sound bold and entirely inconsistent in itself. It is all true. Can we learn to see it? From the military expert to the anthropologist thinking men recognise that for over 100,000 years war has been almost continuous on the earth. The inventors of chipped flint successfully fought those inferiors who had *not experimented* with flint. There were then no better arms. These also got their game even when it was scarce and other means failed, and so they continued to survive. This little and early example of survival was repeated a great many times before our present complex world conditions were reached, and will as surely continue to be repeated. The fundamentals were always the same.

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* From the *Journal of Industrial and Engineering Chemistry*, viii., No. 6.

A 42-cm. gun is only a better flint; trinitrotoluol is only a more modern sling. Arms and ammunition have changed, but just so have also changed the myriads of other important accessories to survival. This is the important point. Good guns go with good clothes, and nitre is good for fertilisers and for gun-cotton. The signs that we are improving in our civilisation will also indicate that we are growing in our powers of national defence, but this should come rather as a consequence than as an object. The world has always been improving, and the real growth and development has come to those nations which have been responsible for the original research work and not for the mere storage or conservation of the knowledge.

The first or fundamental discovery in any series is not the only important one, so I am going to take an extreme view and say, it is only the continuation of research which is of any considerable importance to us. The fundamental discoveries may be like seeds but the values are like growing plants. An acorn may correspond to the work of a Henry or a Faraday, but the great and growing tree of electrical or chemical work corresponds more nearly to the living state of the oak species. We are much more interested in what is to come than in what has already been accomplished.

Problems for Research.

I realise that I ought to illustrate this appeal for research by concrete examples of chemical things to study. I know the feeling of the chemist who is mentally compressed by the mass of investigation work which has already been done and by the known facts which seem already to cover entirely all possibilities, but I know, too, that the future will make use of knowledge for which we now have no *vocabulary* and no powers for comprehension, and so could not possibly *anticipate*. If, then, I try to illustrate the search for new knowledge you may be sure my illustrations will be inadequate.

In the first place I cannot be reckless enough. This I learn from looking backward. I would not have dared suggest that a dozen good men should study the little hydrogen generator of the freshman laboratory to see what was in it. If I had, I suppose I should have suggested a research on pipe organs, because of the singing hydrogen flame, or on bombs, because of the explosions. But someone tried synthetic ammonia, others Zeppelins, and others the cutting and welding of iron. When I see in our own factory the threescore men now using oxyhydrogen all day for this latter use I am impressed with the eternal proximity of new and useful knowledge. A very few years ago two or three times as many men would have been necessary to do this work in the old, more difficult, and less satisfactory manner.

The most natural suggestions for research are those simple ones referring to chemical elements. There are still plenty of "unknowns" among the elements, and of one thing we may be sure, there are certainly no two alike. Any chemist who wants to add to chemical knowledge need not go beyond the list of elements for his subject. The properties he discloses will every one of them be some time a help to his science and of service to his country. As far as possible, also, his country will reward him with patents if he asks them.

We ought to begin at the points where others left off and continue the research of the chemical elements. One reason why this appeals to me is that I have seen so many recent applications of entirely new knowledge of elements in my own work. I merely mention tungsten, molybdenum, boron, argon, silicon, magnesium, titanium, thallium, vanadium, and chromium, which, because of properties not known until recently, are nevertheless already doing commercial service in our restricted electrical field. Surely we know still far too little about these elements, but we know less about many others.

If now the chemist, still neglecting the infinite compounds and narrowed in his researches to the elements, and then perhaps to the metals, and finally to a single element, still asks "What shall I do?" I would refer him to the isotopes of his element. Our American Richards, supporting the researches resulting from the studies of radio-activity, has shown that there are two leads. They are somewhat different but cannot be separated easily. Of course some one ought to separate all isotopes, and then there is plenty of room for research on the single isotope.

One of the great needs of the country which reflects on us chemists and calls for immediate research is that for American potash. There is no supply in sight which is nearly comparable with the German deposits, and our fertiliser and other industries will certainly suffer because of this difference. We have plenty of felspar calling for a simple process for removing the potash it contains. We have oceans of sea-water carrying plenty of potash. We don't know how to extract it. Don't say it can't be done, for it is being done by miles of seaweed. Why should we confine ourselves to trying to take it away from the seaweed instead of learning what the seaweed knows about getting it from the water? You may look supercilious, but until a large number of chemists have studied semi-permeable membranes there will always be this lack of understanding of those simple reactions of living matter going on around us. There will always seem to me a possibility of doing such physical and chemical things more nearly as we may wish to do them when we know how they operate.

When nothing new is being done by us it will be a sure token of our decay. When we stop increasing our experimental activities or fall for a considerable time behind the activities of other countries we may expect to see our light become merely a memory, like that of Greece or Rome. Thus far we Americans have not reached a fair average as investigators in natural sciences, and yet we have incomparably superior conditions for the growth of research. I cannot look beyond the period when research shall cease in a country and still imagine that country a power in the world.

There are no sharp lines to be drawn through research to separate pure from applied, scientific from practical, useful from useless. If one attempts to divide past research in such a manner he finds that time entirely rubs out his lines of demarcation. At this particular time, however, one may imagine a more or less zigzag zone which serves to divide research in a commonly accepted way. I will illustrate. In a manufactory the price of a new product should include the cost of research. No matter how complicated the system this is always true, otherwise the industry would ultimately commit suicide. In practice it is common to apportion to particular products the cost of their separate development, and to fix the price so that within a reasonable time or by a reasonable volume of sales the so-called development cost may be wiped out; thereafter the product may be sold on the basis of the continuing cost of actual production. While this system is extensive it does not cover the cost of many of those original researches which may have been absolutely necessary. The argon tungsten lamp in its development cost did not carry the expenses of Rayleigh and Ramsay's work, and there will probably always be such classification of research work necessary.

"Unpaid Research" needs Appreciation.

Under such a classification the part of research I am most interested in promoting is what we may call the *unpaid* kind, not because it is cheapest but because it is the most valuable. It is most neglected, most poorly understood, most in need of appreciative support in America.

The separate industries do not need encouragement in research nearly so much as the nation needs it. The industries can be depended on to estimate its value to them, for they take annual inventories, but a country which keeps no books seems to have to depend on accident for its most valuable research work.

It seems to me that many of our American colleges have been shortsighted in this respect. This may be explained by the rapidly increasing demand in our growing industries for analytical chemists and chemical engineers, who could at once meet the existing industrial requirements. This demand has kept the chemical departments of our colleges and technical schools very busy with the elementary and analytical side of chemistry, and left little room for the synthetical or experimental side. It has also naturally tended toward the development of highly efficient organisations, equipments, and corps of instructors for the preparation of the one type of chemist, but this very success seems frequently to make impracticable the training of men for research. The conscientious American professor has usually devoted his life to bringing his students up to a certain promising stage of interest in science and experiment only to see them scatter before they have had any experience in questioning nature or have tried any unbeaten path of chemical byway.

While I am greatly interested in what might be done for science by technical research laboratories in the industries, I am sure that the university must be the important factor in guiding the pioneer work if we are to be a sufficiently advancing nation.

Let me recall recent words of President Wilson:—

"I know I reflect your feeling and the feeling of all our citizens when I say the only thing I am afraid of is not being ready to perform our duty. I am afraid of the danger of shame. I am afraid of the danger of inadequacy. I am afraid of the danger of not being able to express the correct character of the country with tremendous might and effectiveness whenever we are called upon to act in the field of the world's affairs."

These words ring true. The American spirit is characterised by them. But think further a moment. They refer to a fear based upon an entirely corrigible defect. The cure is in our hands. The time when we are called upon to act in the field of the world's affairs is *now*, but it was yesterday, and it will be to-morrow. I maintain that no nation can effectively act in that field at odd or selected moments. It is either doing it much of the time or it is kely to be unable to do it any of the time.

ESTIMATION OF SELENIUM IN SULPHUR.

By W. SMITH.

The separation used depends upon the facts that the bromides of sulphur and selenium when shaken with excess of cold water decompose according to the following equations:—

$$2S_2Br_2+3H_2O = H_2SO_3+3S+4HBr,$$
$$SeBr_4+3H_2O = H_2SeO_3+4HBr,$$

and that the decomposition of the selenium compound proceeds very rapidly compared with that of the sulphur compound.

When the acids of selenium (small amounts of selenic acid being present, due to oxidation of selenious acid, by bromide water) are heated with excess of hydriodic acid they are reduced to selenium as follows (A. W. Pearce, *Research Papers of Kent Chemical Laboratory*, 1901, i., 338):—

$$H_2SeO_4+6HI = 4H_2O+3I_2+Se,$$
$$H_2SeO_3+4HI = 3H_2O+2I_2+Se.$$

In order to test the completeness of the above reaction a standard solution of selenic acid was prepared from selenium purified from four precipitations, and the selenium contained was estimated as described below, with the following results:—

	1.	2.	3.	4.
Selenium added (grm.)	0·0160	0·0586	0·0586	0·0586
Selenium found (grm.)	0·0158	0·0590	0·0590	0·0590

The details of the method, based upon the above reactions, are as follows:—Weigh a quantity of finely-ground sulphur (preferably about 50 grms.) into an Erlenmeyer flask, then add a few cc. more bromine than grms. of sulphur used; allow to stand for fifteen minutes (it is advisable to conduct this work in a fume cupboard in which a little ammonia has been sprinkled).

Transfer to a 100 cc. separating funnel, and shake vigorously with 40 cc. of bromine water for one minute; separate the sulphur bromide from the aqueous solution, and pour the latter through a wetted filter-paper. Add about 2 cc. of bromine and 40 cc. bromine water to the sulphur bromide, and repeat the extraction four times, the last extract being kept separate. If insufficient bromine be added sulphur separates during extraction; this can be avoided by the addition of more bromine to the sulphur bromide. If the quantity of sulphur in the aqueous solution be small it can be removed by boiling the bromine water.

The last extract is treated in the same way as the combined first extractions (proportionate amounts of potassium iodide and hydrochloric acid being used). If the presence of selenium be proved in this last portion, extraction is repeated as often as necessary.

The solutions, which must contain an excess of bromine, are boiled till clear; any remaining free bromine is removed by careful additions of powdered potassium metabisulphite, or sulphite, until the solution just becomes colourless. The selenium in the red form may commence to precipitate at this stage.

Dilute to about 250 cc., add 15 cc. of hydrochloric acid, and about 5 grms. of potassium iodide, and boil; this completes the precipitation of the selenium, and gradually converts the red into the black allotrope.

The free iodine is removed by the addition of a few cc. of the solution of potassium metabisulphite or sulphite. Boil for twenty minutes, filter through a tared Gooch crucible, wash the selenium with hot water, and dry at 100° C. until a constant weight is obtained.

The method has been found to work successfully on standard sulphur samples which were prepared as follows:—

No. 1. By mixing red selenium with sulphur.
No. 2. By mixing black selenium with sulphur.
No. 3. By melting black selenium with sulphur.
No. 4. By melting black selenium with arsenic and sulphur in the molecular proportions of As_2SSe_2.

The following results were obtained by the above method with from 10 to 30 grms. of the standard sulphur samples:—

No. 1.—*Red Selenium mixed with Sulphur.*

Amount added. Grm.	Amount found. Grm.	Error.
0·0454	0·0465	+0·0011
0·0405	0·0410	+0·0005
0·0454	0·0460	+0·0006

No. 2.—*Black Selenium mixed with Sulphur.*

Amount added. Grm.	Amount found. Grm.	Error.
0·0390	0·0390	—
0·0488	0·0493	+0·0005
0·0341	0·0338	−0·0003
0·0488	0·0497	+0·0009
0·0488	0·0488	—
0·0219	0·0212	−0·0007

No. 3.—*Black Selenium melted with Sulphur.*

Amount added. Grm.	Amount found. Grm.	Error.
0·0227	0·0220	−0·0007
0·0488	0·0478	−0·0010
0·0488	0·0492	+0·0004
0·0171	0·0171	—
0·0488	0·0490	+0·0002
0·0244	0·0250	+0·0006

No. 4.—*Black Selenium melted with Arsenic and Sulphur in Molecular Proportions of* As_2SSe_2 *and then mixed with Excess of Sulphur.*

Amount added. Grm.	Amount found. Grm.	Error.
0·0244	0·0252	+0·0008
0·0488	0·0496	+0·0008
0·0488	0·0495	+0·0007
0·0283	0·0280	−0·0003
0·0464	0·0470	+0·0006

A number of samples of commercial sulphur were analysed, and the following are some of the results obtained from Japanese samples:—

Per cent arsenic.. ..	0·80	0·70	0·50	0·30
Per cent selenium ..	0·152	0·085	0·055	0·045

It will be noted that there would appear to be a certain parallelism between the amounts of arsenic and selenium present in the above samples.

Tellurium, if present, will be estimated as selenium by this method, but examination of several samples of crude selenium obtained from sulphuric acid chambers proved that it was present in very small quantity, if at all, the maximum being 0·1 per cent of the selenium present.

The method used for the determination of tellurium was that of Browning and Flint which is given below (*Am. Journ. Sci.*, [4th Series], 1909, xxviii., 112). If a sample of sulphur containing both selenium and tellurium be encountered, they could be estimated by the method described for the estimation of selenium, and tellurium could be determined as follows:—

Dissolve the mixed selenium and tellurium which is contained in the Gooch crucible in a small quantity of hot strong nitric acid; gently evaporate the solution just to dryness; dissolve the mixed oxides of tellurium and selenium in a small quantity of 1 : 2 hydrochloric acid, and warm for a few minutes. Dilute this solution with 200 cc. of boiling water, and add ammonium hydroxide in very slight excess, then make very slightly acid with a drop or two of acetic acid, allow to stand for thirty minutes, and cool.

Now decant the liquid through a tared Gooch crucible, and wash the tellurium dioxide with cold water, and dry at about 110° C. until constant weight is obtained.—*Journal of Industrial and Engineering Chemistry*, vii., No. 10.

THE REDUCTION TEST FOR TUNGSTEN.

By M. L. HARTMAN, Professor of Chemistry South Dakota School of Mines, Rapid City, South Dakota.

The recent activity and interest in tungsten has brought to our attention the methods for detecting this element. One frequently hears the remark that the qualitative tests are uncertain, and it was due to such a remark that this investigation of the sensitiveness of the reduction test for tungsten was begun.

Tungsten minerals when fused with an excess of sodium carbonate give soluble sodium tungstate (Na_2WO_4). When solutions of sodium tungstate are made acid with hydrochloric or sulphuric acids, in the cold, a white flocculent precipitate is formed (composition varies from $WO(OH)_4$ to $WO_2(OH)_2$ which on heating becomes yellow tungstic acid or oxide (WO_3 or H_2WO_4). If a strong reducing agent is added, the solution is changed to a bright blue colour, due to a suspension of a finely divided, flocculent precipitate, consisting of oxides of composition between WO_3 and WO_2 (sometimes given as $W_2O_5W_3O_8$, W_4O_{11}). If the reduction is carried still further, the brown tungsten dioxide (WO_2) is formed. This change was very slow at room temperatures, the blue precipitate having been kept for two days.

A rather extended investigation was made of the best method for making this qualitative test. For studying the reactions involved, a dilute standard solution of sodium tungstate was prepared. In brief the following results were obtained:—

Effects of Different Reducing Agents.

The reducing agents usually recommended for this test are zinc and hydrochloric acid, tin and hydrochloric acid, and stannous chloride and hydrochloric acid. It was found that the use of tin and hydrochloric acid was the most satisfactory, as the evolution of hydrogen gas was not too violent, and the reduction was very rapid, due to the quadrivalence of tin. The use of zinc and hydrochloric acid was fairly satisfactory, but not as desirable as tin. The evolution of hydrogen was frequently so violent (in the concentrated acid solution required for the best results) that the blue colour could not be detected in the solution. Furthermore, with very small amounts of tungsten the reduction was carried to the brown colour so rapidly that the blue colour escaped notice.

The use of stannous chloride in hydrochloric acid solution is not to be recommended for this test. The blue colour was sometimes obtained when the concentration of the tungsten was high, when the amount of stannous chloride was large, and when the solution was heated for some time. Small quantities of tungsten could not be detected, using this reducing agent.

Hydrogen peroxide is sometimes used as a reducing agent in similar reactions. It was found that it did not reduce tungstic oxide either in the cold or when heated.

Oxalic acid is also used occasionally. This reducing agent was without effect on tungstic oxide.

The Effect of Acid Concentration.

Using zinc as the reducing agent, and hydrochloric acid at room temperature, and sodium tungstate solution equivalent to 0·01 grm. of WO_3, in a total volume of 10 cc., the blue colour became distinct with 0·25 cc. concentrated hydrochloric acid in one hour; with 0·50 cc. concentrated hydrochloric acid, in two minutes; with 1·00 cc. concentrated hydrochloric acid, practically instantaneously.

Amounts of Tungstic Oxide which can be Detected.

In a total volume of 2 cc., with ½ cc. of concentrated hydrochloric acid, and with tin or zinc as the reducing agent, 0·0005 grm. of WO_2 could easily be detected by the blue colour. Using tin, the colour was produced in the cold, while with zinc it was necessary to heat the solution to get an immediate colour. If allowed to stand at room temperature, the blue colour could be detected in half an hour.

Thus in solutions containing only tungsten salts the test is very sensitive. As small an amount as 1 mgrm. of WO_3 may easily be detected.

The above experiments were made upon pure sodium tungstate. In order to study the reduction test under actual conditions, ores of known tungstic oxide content were examined. Here, before the reduction test can be applied, the material must be brought into solution as a tungstate, or in the form of tungstic oxide in finely divided or colloidal particles. There are two methods which can be used—fusion with sodium carbonate and subsequent solution, or solution of the ore in hydrochloric acid.

The following ores (Table I.) were tested by both methods and the tabulated results obtained:—

Table I.—*Reduction with Tin after Fusion.*

Material.	Per cent WO_3.	Solution in HCl.	Solution in HCl.
Wolframite sand ..	3·0	No colour	Strong blue
Wolframite ore ..	16·0	Strong blue	Residue blue but not solution
Wolframite concentrate	32·0	,,	Distinct blue
Sheelite ore	38·0	,,	No colour
Wolframite concentrates	68·0	Blue residue and faint blue solution	Strong blue
Sheelite	75·0	Strong blue	Distinct blue solution and blue residue

From the tests made on these tungsten materials it was found not safe to depend upon a single method for all cases. Most of the ores dissolve sufficiently in boiling hydrochloric acid to give the blue colour on reduction. The low-grade ore did not respond to this treatment. In the method of fusion with sodium carbonate it was found essential to have a large excess of sodium carbonate. This is to ensure the complete transformation to soluble sodium tungstate. It was further found that for the most accurate tests the fused mass should be first dissolved in water and then made acid with hydrochloric acid. The reason for this procedure is to ensure a colloidal precipitate of the tungstic oxide, which on reduction gives the blue solution rather than the blue residue which forms when the fusion is dissolved in hydrochloric acid.

In conclusion, the following general directions can be recommended for testing for tungstic oxide in ores. Boil at least 0·2 grm. of finely divided material in a small test-tube with concentrated hydrochloric acid until about one-half the acid is evaporated. Dilute with an equal volume of water, add a piece of metallic tin (mossy), and heat if necessary. A fine blue colour indicates the presence of tungsten. If this test gives negative results, about 0·5 grm. of the material should be fused in at least 4 grms. of sodium carbonate. (This may be done with an ordinary Bunsen burner in a metal crucible, or before the blast in a porcelain crucible). Dissolve the fused mass by boiling water in the crucible. Acidify the aqueous solution with an equal volume of concentrated hydrochloric acid, add a piece of metallic tin, and warm if necessary. The volume of the solution should not be more than 10—20 cc. A fine blue colour indicates the presence of tungsten. In either case if reduction is continued long enough a brown colour is obtained.

These tests if properly used will show the presence of tungstic oxide in materials as low as 2 per cent, and by using special precautions will detect tungsten in even lower grade materials.

(Note.—The interfering colours which might be produced by other elements present, under the conditions of the test for tungsten, are being studied at the present time. Columbium (niobium) gives a blue colour which is said to disappear on dilution and which does not become brown after long reduction. Vanadium also gives a blue colour on reduction, but tartaric acid will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum on reduction goes through a series of colour changes from violet to blue to black. Titanium gives a violet colour. No other elements are likely to interfere with the test for tungsten.—*Pahasapa Quarterly*.

A NEW METHOD OF INJURING OUR FIGHTING MEN ON THE CONTINENT.

A lady correspondent asks for the following information, which we shall be very glad to receive :—

Being in touch with a number of hospitals, I find that many of our soldiers are burnt, not only by the jets of liquid fire, but also by being first powdered over and then having water sprayed over them, burning their clothes, their faces, and wherever else the powder catches them. I cannot remember the name of the "powder" used, but am anxious to find out what can neutralise the terrible effect created by this combination. Our soldiers seem to have no protection as yet, and I hope that some protection may be possible. Is there no chemical that can save them? Is it the chemical action of the water on the "powder" that causes the burning? Can our men be saved by prepared veils or by spraying?

Is there anything a mere woman can do in this matter? I am trying to help where I can, and when one hears of burnt eyes and all that horror added to shell and shot one longs to be able to save them something at least. In this war every inventive faculty seems to have been utilised. On the one side hell is created, therefore saving and healing on the other must follow, but unfortunately the evil seems easier to invent and perfect than the remedies. What can be done?

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 29, 1916.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read :—

"*Determination of Gravity at Sea.*" By Prof. Arthur Schuster, Sec. R.S.

Dr. Duffield has recently described some preliminary experiments on the measurement of gravity at sea by means of a new method which had originally been suggested by Hecker, and which, in the main, consists in balancing the pressure of a column of gas kept at constant temperature and that of a column of mercury the length of which can be indirectly determined. The results are very promising, but as the ultimate success of the method must depend on the elimination of errors due to unavoidable disturbances, it seemed advisable to discuss the theory of the apparatus a little more fully.

The present paper deals more particularly with the effects of the forced oscillation of the mercury due to the vertical motion of the ship, but other sources of error are also considered. These errors are much affected by the cross-sections of the two branches of the barometer tube. In order to reduce the effect of the vertical motion of the ship, these cross-sections ought to be as large as possible, but a limit is set to their areas by the consequent increase of the quantity of mercury necessary for the temperature correction. Constructional considerations render it necessary to have the area of that branch of the barometer system which is kept at constant pressure larger than that of the branch which is kept at zero pressure, but this increases the error due to the uncertainty of the electric contact.

The most advantageous relative dimensions of the different parts of the apparatus therefore depend on the accuracy with which the electric contact is established and on the degree to which the mass of mercury in the apparatus can be kept at uniform temperature. Attention must also be given to the method of suspension, as the most dangerous source of error—because difficult to correct—is the inclination of the barometer system to the vertical.

"*Genesis of Pleochroic Haloes.*" By Prof. J. Joly, F.R.S.

Both uranium-radium and thorium haloes develop according to the same laws; certain internal structures appearing first in the form of ring haloes. The addition to these of the outermost feature due to RaC or ThC_2 appears at an early stage. Intermediate details then follow. It is clearly shown that some cause exists to modify the effects of the divergence of the rays outwards. It is suggested that "reversal" of the effects of the earlier ionising stimuli by subsequent ones of different intensity—such as occurs in photo-sensitive media—would afford an explanation of the evasion of the inverse square law.

Basing the genesis of the halo on the addition of parallel rays of the ranges concerned, very perfect agreement between theory and observation is obtained in the case of the thorium halo. In the case of the uranium-radium halo, the outer features are also in good agreement with theory, but the features referable to rays of shorter range are not reconcilable. Thus the inital halo-ring is too great in radius to fit the curve which would be derived from the existing knowledge of the ranges.

Haloes derived from emanation of radium as primary substance have been identified. And also what appears to be "reversed" haloes.

"*Some Determinations of the Sign and Magnitude of Electric Discharges in Lightning Flashes.*" By C. T. R. Wilson, F.R.S.

Measurements have been made of the sudden changes produced in the potential gradient at a point on the earth's surface by lightning discharges, the approximate distance of the discharge being in many cases determined by timing the resultant thunder.

The method used in the determination of the sudden changes of potential gradient serves also for absolute measurements of the potential gradient and the earth-air current. It depends upon the measurement of the quantities of electricity which pass between an exposed conductor and the earth through a suitable measuring instrument, such that the potential of the exposed conductor never differs from zero by more than a few thousandths of a volt.

A special type of capillary electrometer has been found, suitable for the purpose. The exposed conductor has generally consisted of what is substantially a mass of earth with its flat upper surface on a level with the surrounding ground.

When a discharge to earth is sufficiently distant, its electric moment—the product Q H of the quantity of the electricity discharged and the mean height from which it has been derived—may be taken as being given by $\frac{1}{2}FD^3$, where F is the resulting change in the electric field at the place of observation and D is the distance of the discharge. Observations of the effects of discharges at different distances, too small for the above relation to hold, give information as to the values of each of the factors Q and H.

The results of one thunderstorm (August 15, 1915) may be interpreted as indicating that the discharges were nearly all approximately alike, Q being about 33 coulombs and H of the order of 10 kilometres; the range of variation in the distances of the discharges was not quite sufficient to decide whether the discharges reached the earth's surface or not, but the value of Q is practically the same on either view.

"*Kinetic Theory of a Composite Monatomic Gas: Diffusion, Viscosity, and Thermal Conduction.*" By S. Chapman.

"*Further Observations on Protozoa in Relation to Soil Bacteria.*" By T. Goodey, D.Sc.

"*New Bennettitean Cones from the British Cretaceous.*" By M. C. Stopes, D.Sc.

"*Phenomena Relating to the Spectra of Hydrogen and Helium.*" By T. R. Merton and J. W. Nicholson.

1. A method has been found for the accurate determination of the photographic intensities of spectrum lines and the reduction of such intensities to absolute values by comparison with the continuous black-body radiation of the carbon arc.

2. A study has been made of the relative intensity distribution in the spectra of helium and hydrogen under different conditions of excitation.

3. It has been found that under certain specified conditions there is a transfer of energy from the longer to the shorter wave-lengths in any given series, and that, under such conditions, the associated series, and in particular the Diffuse series, are relatively enhanced at the expense of the Principal series.

4. It has also been found that the distribution of intensity found in certain celestial spectra can be approximately reproduced in the laboratory.

5. A study has been made of the separations of the components of lines of the Balmer series of hydrogen, and the mean values of the separations of the doublets constituting the lines H_α and H_β have been found to be respectively 0·132 A.U. and 0·033 A.U. These values are consistent with the separations appropriate to a Principal series, and the first is in precise agreement with the value deduced by Buisson and Fabry.

"*The Period of a Spherical Resonator with a Circular Aperture.*" By F. P. White.

"*Rôle of the Blood Fluids in the Intraleucocytic Digestion.*" By Capt. S. R. Douglas, M.R.C.S., L.R.C.P.

OBITUARY.

Prof. ELIE METCHNIKOFF.

We regret to have to announce that the death of Prof. Elie Metchnikoff took place at the Pasteur Institute, at Paris, on July 15, after an illness of some months.

The late Prof. Metchnikoff was born of Russian parents in 1845. His birthplace was Ivanavka, in the Russian province of Kharkoff, and he received his early education first at the Lyceé at Kharkoff, afterwards graduating at the University. He then spent some time in Heligoland studying marine organisms, and afterwards worked under Leuckhart, first at Giessen and then at Gottingen. After some time spent in a laboratory at Naples he returned to Russia and taught at Odessa and at Petrograd. In 1870 he was appointed Professor of Zoology and Comparative Anatomy at Odessa. Twelve years later, on the assassination of the Tsar Alexander III., he left Russia, going first to Messina, where he began some of his most important work on phagocytosis. This he continued for a short time after returning to Odessa, where he established a new bacteriological laboratory; but his work had brought him to the notice of Pasteur, who offered him accommodation and every assistance at the recently established Institut Pasteur. Here he remained actively working almost up to the time of his death.

Metchnikoff's early work on pure zoology, which included the study of the embryology of Ctenophora and the investigation of the Cecidomyia larva, proved him to be an acute observer and an enthusiastic and painstaking worker. It is, however, as a pathologist that his name will live. While at Messina his attention was directed to the study of the function of the colourless corpuscles or phagocytes of the blood and lymph, and he showed that they possess the power of engulfing and destroying many micro-organisms. He believed that phagocytes have been evolved by natural selection in the animal organism, and he worked out the theory that immunity to infective disease is due to the activity of the phagocytes of the animal. He evolved a theory of inflammation which finally destroyed the older ontological conceptions, and his work on the dynamical side of histology may almost be said to have opened up a new era. At the Pasteur Institute he made a special study of the bacteria of the alimentary canal, and he advocated the use of soured milk as a cure for intestinal troubles, thus introducing the "tame" lactic acid bacilli to overcome the "wild" microbes, as he called them. Metchnikoff's work on longevity attracted much attention. He believed that one of the prime causes of senile degeneration is autointoxication, and he advocated direct measures against intestinal putrefaction to lengthen life. He laid stress upon the distinction between the average longevity of a species and its normal specific longevity, which he believed differed very widely.

Prof. Metchnikoff's publications include an epoch-making discussion of Intracellular Digestion, which appeared in 1882, and a monograph on "The Struggle of the Organism against Microbes," in which the theory of phagocytosis was explained in detail. In 1892 he wrote a treatise on the "Comparative Pathology of Inflammation," in which it was shown that inflammation is the result of the collection of hosts of scavengers at an injured or diseased part. His greatest work was entitled "Immunity in Infectious Diseases" (1901), and contained a complete exposition of his theory of immunity. A popular work entitled "The Nature of Man," published in 1903, in which his views on longevity were discussed, attracted much attention and was widely read. Metchnikoff was highly esteemed by the scientific men of all nations, and scientific societies had bestowed many honours on him. He received the Nobel medal and prize for his work on immunity, and the Copley Medal of the Royal Society. The value of his services to humanity needs no emphasising.

He possessed in a high degree all the attributes of the truly great scientific man. His imagination was vivid, but he was a careful experimenter and spared no pains in the accumulation of facts upon which to base his theories. He was full of enthusiasm for the acquisition of knowledge for its own sake, but at the same time the benefits to humanity of the application of scientific methods and knowledge were never absent from his mind. In spite of his advanced years he had been working at the Pasteur Institute on questions relating to the health of armies, and his death will be deeply felt by all who have at heart the advancement of knowledge and the progress of civilisation.

NOTICES OF BOOKS.

A Senior Experimental Chemistry. By H. E. Dunstan, D.Sc. (Lond.), F.C.S., and F. B. Thole, D.Sc. (Lond.), F.C.S. London: Methuen and Co., Ltd. 1916. Pp. xiii. + 522. Price 5s.

Students in the upper classes of schools and in technical colleges will find this a useful text-book. It covers the whole of inorganic chemistry, but is not intended to be used by beginners, nor is the arrangement of the subject matter that which the teacher or student would naturally follow. The first part is entirely theoretical and deals satisfactorily with the laws of chemical combination, the gas laws, solutions, electrolysis, thermo-chemistry, &c. The course of experimental work provided is good, although in some cases the directions given would require supplementing, as, for instance, when the student is simply told to "reduce it in a current of coal-gas in Experiment 3." After the theoretical part a systematic treatment of the elements classified in accordance with the Periodic System follows. Good detailed accounts are given of the properties of the elements and of their chief compounds, and many experiments, such as the student could perform for himself with comparatively simple apparatus, are described. Many useful schemes and tables are provided, and the book will undoubtedly be of great assistance to candidates for examinations. Qualitative analysis and some volumetric work are included, so that a complete course of practical as well as theoretical work is provided.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 21, May 22, 1916.

Effect of Temperature on the Structure of Paraffins. —Thadée Peczalski.—The density of pure paraffin varies from 0·848 to 0·875, but the author has found that some specimens have a density higher than 0·900. This may be supposed to be due to the presence of impurities, or another explanation may be given. The author has observed that when paraffin is heated in a test-tube for some time to a temperature below its melting-point it undergoes transformations, excavations becoming apparent throughout its mass. A paraffin of density 0·875 had density 0·900 after being heated for twenty-four hours. It also became translucid, while it was almost opaque before heating. The transformation is accompanied by a great diminution in the electric conductivity. Microscopic examination shows that heating induces crystallisation of the superfused parts, increases the size of the crystals, and possibly changes their orientations.

Existence of a New Group of Lines (Series M) in High Frequency Spectra.—Manne Siegbahn.—The researches of Barkla and others have shown that the high frequency spectra of the chemical elements are composed of two groups of rays (Series K and L) which differ considerably in their power of penetration. Many authors have supposed that other series (J, M, &c.) exist, but hitherto no experimental confirmation of this supposition has been brought forward. In a series of systematic researches on the spectrum of uranium the author has observed a new group of lines which correspond to the hypothetical series M. Owing to the great absorption of these rays by air the spectrograph had to be placed in a vacuum, and the crystal employed was a plate of gypsum. The examination of the elements Th, Bi, Pb, Tl, Au showed that the series was represented in spectra of all of them.

New Method of Estimating Fluorine.—F. Pisani.— When thorium nitrate is added to a solution of an alkaline fluoride, slightly acidified with acidic acid or by nitric acid, a precipitate of thorium fluoride is obtained ($ThF_4 + 4H_2O$). It is gelatinous like alumina and very voluminous, and so heavy that it rapidly settles. The supernatant liquid is limpid, and the end of the reaction may be ascertained by pouring it off into a conical flask. Too large an excess of the reagent must not be added, for in a concentrated liquid thorium nitrate may dissolve a little of the precipitate. When the amount of fluorine present is known roughly it is best to weigh the necessary quantity of solid reagent and dissolve in water. The reaction is very sensitive, and less than 0·01 per cent of fluorine can be detected by it. As thorium fluoride loses a molecule of water at 100° it can be weighed after desiccation and the amount of fluorine deduced. It is better to incinerate with the filter and heat strongly; thus the thoria, ThO_2, is obtained which gives the amount of fluorine in the ratio $\frac{ThO_2}{4F}$. Insoluble fluorides can be fused with sodium carbonate and phosphates containing fluorides with silica and sodium carbonate.

MISCELLANEOUS.

Institute of Chemistry.—*Pass List, July* (1916) *Examinations.*—The results of the Examinations of the Institute of Chemistry recently held in London have now been published. Five candidates passed the Intermediate Examination, viz.:—A. C. Francis, Miss P. L. Garbutt, A. J. Hall, B.Sc. (Lond.), H. J. Hegan, B.Sc. (Lond.), and J. Sandilands. Nine candidates passed the Final (A.I.C.) Examination, viz.:—In the Branch of Mineral Chemistry: E. G. Macintyre, B.Sc. (Glas.), and A. Stewart, B.Sc. (Glas.); in the Branch of Organic Chemistry: P. J. Brannigan, M.Sc. (Q.U.B.), T. Hopkins, B.Sc. (Lond. and Wales), D. Madden, A.R.C.S.I., James Ogilvie, B.Sc. (Edin.), and E. E. Wells, B.Sc. (Lond.); in the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water: H. E. Cox, B.Sc. (Lond.), and T. L. McEwan, B.Sc. (St. Andrews). One candidate examined for the Fellowship also took the Chemistry of Food and Drugs, &c., and passed: J. Wood, M.A , B.Sc. (Aberd.).

NOTES AND QUERIES.

The Weed called "Couch."—(Reply to H. M. Gledstone).— Mr. Gledstone will find an article on the composition and agricultural value of couch and couch ashes in the 1897-8 volume of the *Journal of the Bath and West of England Agricultural Society*, by John Hughes, F.I.C., Agricultural Analyst for Herefordshire.

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THE CHEMICAL NEWS

VOL. CXIV., No. 2958.

TWENTY-THIRD ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1915.*

By GREGORY PAUL BAXTER.

THE number of new researches upon the atomic weights published during the past year is as large as could be expected under prevailing conditions.

For the first time since 1912 the International Committee on Atomic Weights (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2449) recommends changes in the accepted values for a few elements. These changes are given in Table I.

TABLE I.

	1912.	1916.
Carbon	12·00	12·005
Sulphur	32·07	32·06
Helium	3·99	4·00
Tin	119·0	118·7
Lead	207·10	207·20
Radium	226·4	226·0
Uranium	238·5	238·2
Ytterbium . ..	172·0	173·5
Praseodymium .	140·6	140·9
Yttrium	89·0	88·7
Lutecium.. ..	174·0	175·0

Oxygen.—Germann (*Journ. Phys. Chem.*, 1915, xix., 437) discusses critically determinations of the density of oxygen, and describes in detail his own experiments in this field (*Comptes Rendus*, 1913, clvii., 926; see also Twenty-first Annual Report, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 457). His final conclusion is that the weight of the normal litre is 1·42905 grms.

Carbon.—By analysis of the calcium and ammonium salts of salicylic acid and the ammonium salts of *m*- and *p*-oxybenzoic acids Œchsner de Coninck found the molecular weight of these acids to be 137·99 (*Comptes Rendus*, 1915, clx., 67). If H = 1·008, carbon is 11·99. As only four experiments were performed and the quantities used were very small, this result has little significance.

Copper.—Shrimpton (*Proc. Phys. Soc.*, 1914, xxvi., 292) compared the weights of simultaneous silver and copper deposits. The silver cells were of the Guthe-Richards porous pot type. Corrections were made for inclusions in the silver and for cathodic solution of the copper. Vacuum weights are given (Table II.).

Molybdenum.—Müller (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2046) has determined the atomic weight of this element by oxidising weighed amounts of the metal in a current of air and weighing the resulting oxide. The metal was prepared by reduction in hydrogen from oxide which had been fractionally sublimed as hydroxychloride in a current of hydrochloric acid. Quartz apparatus was utilised. Weights are corrected to vacuum (Table III.).

Cadmium.—Œchsner de Coninck and Gérard (*Comptes Rendus*, 1915, clxi., 676) ignited weighed amounts of cadmium carbonate and then reduced the resulting oxide to metal in a current of hydrogen. It is worth noting that an error of 0·1 mgrm. in the weight of the metal would alter the atomic weight by nearly one-tenth of a unit (Table IV.).

Cadmium.—Hulett and Quinn (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1997) have published a paper in support of their earlier work.

TABLE II.

Weight Ag.	Weight Cu.	Atomic weight Cu.
2·21697 2·21636	0·65306 0·65309 0·65305	63·567
4·32294 4·32294	1·27358 1·27341 1·27351 1·27346	63·561
2·18669 2·18601	0·64406 0·64406 0·64416 0·64407 0·64415	63·563
2·14755 2·14747	0·63264 0·63262 0·63255 0·63266	63·559
3·24431 (3·24523)	0·95570 0·95580 0·95581 0·95564	63·561
2·29785 2·29783	0·67673 0·67724 0·67701 0·67718	63·572
3·54120 3·54370	1·04372 1·04339 1·04367 1·04327	(63·558)
3·91789 3·91852	1·15430 1·15434 1·15362 1·15486	63·562
4·83364 4·82973	1·42323 1·42331 1·42331 1·42320	(63·556)
2·43820 2·43837	0·71818 0·71844 0·71828 0·71835	63·562
	Average	63·563

TABLE III.

Fraction.	Weight Mo.	Weight MoO$_3$.	Atomic weight Mo.
I.	0·52591	0·78879	96·027
I.	0·56327	0·84487	96·012
I.	1·12757	1·69117	96·031
II.	0·53014	0·79517	96·011
II.	1·10754	1·66130	96·002
II.	1·62166	2·43181	96·080
II.	1·45530	2·18259	96·047
III.	0·94968	1·42428	96·048
III.	0·65659	0·9870	96·054
Mean			96·035
Mean, omitting the sixth analysis .			96·029

TABLE IV.

Weight CdCO$_3$.	Weight Cd.	Atomic weight Cd.
0·5500	0·3585	112·32
0·6050	0·3943	112·28
0·6600	0·4302	112·32
0·6171	0·4023	112·37
0·5445	0·3549	112·31
	Average	112·32

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* *Journal of the American Chemical Society*, xxxviii., No. 3.

Tin.—Briscoe (*Journ. Chem. Soc.*, 1915, cvii., 63) purified stannic chloride by fractional distillation, the portions analysed being collected in weighed bulbs. After being re-weighed the bulbs were broken under a solution of oxalic and nitric acids, and the chloride was compared with weighed amounts of pure silver. Vacuum weights are given (Table V.).

TABLE V.—Cl = 35·460.

Weight $SnCl_4$.	Weight Ag.	Atomic weight Sn.
9·02435	14·9475	118·685
9·39855	15·5666	118·696
10·32760	17·1058	118·689
9·17005	15·1880	118·699
6·68995	11·0808	118·686
9·33130	15·4570	118·666
7·77450	12·8764	118·702
9·22730	15·2840	118·678
7·55785	12·5183	118·688
9·11535	15·0983	118·683
9·22875	15·2866	118·675
9·21890	15·2696	118·686
11·29055	18·7017	118·675
9·89635	16·3912	118·694
9·43385	15·6250	118·696
	Average..	118·686

Praseodymium.—Baxter and Stewart purified praseodymium material by fractional crystallisation of the double ammonium nitrate (*Proc. Nat. Acad.*, 1915, i., 77; *Proc. Am. Acad.*, 1915, l., 171; *Journ. Am. Chem. Soc.*, 1915, xxxvii., 516; *Zeit. Anorg. Chem.*, 1915, xcii., 171). Each fraction was converted to chloride, which, after fusion in an atmosphere of hydrochloric acid gas, was compared with silver and silver chloride in the usual way. Weights are corrected to vacuum (Table VI.).

TABLE VI.—Cl = 35·457.

Fraction.	Weight of $PrCl_3$.	Weight of AgCl.	Atomic wt. Pr.	Weight of Ag.	Atomic wt. Pr.
3474	4·12848	7·17915	140·913	—	—
3474	6·91605	12·02533	140·939	—	—
3474	7·66554	13·32931	140·923	10·03129	140·943
3474	5·01155	8·71379	140·941	6·55898	140·914
3474	8·78959	—	—	11·50311	140·924
4383	6·04235	10·50744	140·909	7·90820	140·910
4383	6·14745	10·69050	140·902	8·04563	140·914
4381	6·32550	10·99855	140·937	8·27886	140·908
4381	5·12982	—	—	6·71359	140·920
4381	4·59463	7·98940	140·925	6·01331	140·915
4381	4·77556	—	—	6·24994	140·921
4379	5·96661	10·37554	140·913	7·80908	140·910
4379	6·87536	11·95508	140·928	8·99824	140·915
4377	5·73602	—	—	7·50707	140·017
4377	4·64585	8·07758	140·951	6·08029	140·917
4374	6·85492	11·91774	140·965	8·97148	140·916
4374	8·01711	13·93953	140·943	10·49250	140·916
4374	6·17045	10·72833	140·952	8·07425	140·959
4374	6·90040	11·99946	140·911	9·03064	140·926
4374	7·08498	12·32019	140·916	9·27274	140·911
4374	5·81310	—	—	7·60811	140·911
4371	6·20845	10·79552	140·926	8·12541	140·915
4371	7·07590	12·30401	140·924	9·26045	140·922
4368	5·77646	10·04403	140·935	7·56000	140·916
4368	5·72002	9·94631	140·919	7·48596	140·922
	Average	.. ..	140·932		140·919

A very small proportion of cerium in Fractions 4368 and 4371 was quantitatively determined. When a correction is applied for this impurity, the average result of all the experiments is 140·924.

(To be continued).

SOME EXPERIMENTS ON THE EXTRACTION OF RADIUM FROM CARNOTITE ORES WITH CONCENTRATED SULPHURIC ACID.

By HERMAN SCHLUNDT.

AT the present time the carnotite ores of South-Western Colorado and Eastern Utah constitute the principal source of radium in the United States. The carnotites consist of a sandstone with a clay binder variably impregnated with the mineral carnotite, a hydrous potassium uranium vanadate containing barium and calcium.

By boiling carnotite ores with concentrated sulphuric acid the barium and radium compounds present are converted into bisulphates, which remain in solution in an excess of the acid and may then be separated from the insoluble components by filtration, followed by washing the residue with concentrated sulphuric acid. From the acid liquors thus obtained the radium is recovered by diluting with water, whereby barium-radium sulphate is precipitated. The experiments outlined in this paper are based upon the preceding principle.

Partial Analysis of the Ores.

Experiments were conducted with a low-grade and a high-grade ore. Both lots of ore came from the carnotite deposits in the Paradox Valley, South-Western Colorado. A stock of 250 kilogrms. of low-grade ore was available and 5 kilogrms. of high grade. The low-grade ore was sampled and ground to pass through a 20-mesh sieve in the plant of a commercial ore grinding and sampling firm. The high-grade lot of ore was ground and composited with the ordinary laboratory appliances until it passed through a 40-mesh sieve.

Determinations of the valuable constituents of the ore—radium, uranium, and vanadium—seemed sufficient for our purpose. These analytical results appear in Table I. and refer to the air-dry ore as it was used in the experiments. Uranium and vanadium are reported in the customary way as the oxides U_3O_8 and V_2O_5 without implying that these elements are found in this form in the ore:—

TABLE I.—*Uranium, Vanadium, Radium Content of Ores.*

Carnotite.	Per cent U_8O_8.	Per cent V_2O_5.	Moisture at 110°.	Radium parts per billion.	Radium calculated.
Low grade ..	1·66	4·03	1·36	4·88	4·69
High grade ..	14·39	9·67	—	42·78	40·66

The method of analysis followed in the determination of uranium and vanadium in the ores is described in *Bull.* No. 70, U.S. Bureau of Mines (Moore and Kithill, *Bull.* 70, Bureau of Mines, 88, 1913), and by Lind and Whittemore in their investigations on the radium-uranium ratio in carnotites (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 2076). I am indebted to Mr. H. H. Barker for the uranium and vanadium determinations in the sample of low-grade ore.

The determination of radium in the ores and the crude barium-radium sulphates separated from them in the course of the experiments was conducted electroscopically by the emanation method. The emanation was generally separated from the ore samples by boiling suitable quantities with nitric acid after the samples had been sealed up for a month or longer to attain equilibrium with the emanation that diffuses away continuously under ordinary conditions. Proper measurements of the ionisation current produced by the emanation in a standardised air-tight electroscope furnish the data required for computing the quantity of radium.

The radium values found directly by experiment appear in the fifth column, and it is seen that these are approximately 5 per cent higher than the calculated quantities of the last column, which were computed by multiplying the uranium content by the equilibrium ratio of radium to uranium—$3·33 \times 10^{-7}$ (Heimann and Marckwald, *Jahrb.*

d. Radioakt. u. Electronik, 1913, x., 299). Differences of this magnitude are not at all uncommon for small lots of ore, and have been shown to occur occasionally in ton lots of well sampled ore (*cf.* Lind and Whittemore, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 2080).

Our ore samples exhibit the characteristic high emanating power of carnotites; at room temperatures the low-grade ore continuously loses 35·2 per cent of its emanation, the high-grade ore 20·2 per cent.

The determination of radium in the crude sulphates and a few of the ore residues (tailings) was conducted for the most part by fusion of weighed samples with mixed carbonates of sodium and potassium followed by solution of the products in nitric acid, or a second fusion, after the lapse of a known period of storage extending over a few days. The emanation that accumulates during the interval, when collected quantitatively and transferred to a standardised electroscope, can be accurately determined by properly measuring the ionisation current produced. From the data thus obtained the quantity of radium in the sample is readily deduced.

(For details of operation, apparatus, and formulæ used in the calculations, see among other references, Schlundt and Moore, *Journ. Phys. Chem.*, 1905, ix., 320; Randall, *Trans. Am. Electrochem. Soc.*, 1912, xxi., 463; Lind and Whittemore, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 2062; Schlundt, *Trans. Am. Electrochem. Soc.*, 1915, xxvi., 163).

In a few of the radium determinations potassium bisulphate was substituted as a flux for the mixed carbonates. In most of the experiments the percentage extraction of radium from the ore was determined by comparison of the alpha radiation from equal surfaces of ore and tailings spread out in thin layers on very shallow trays.

Treatment of the Ores.

Various experiments of a preliminary character were conducted with 100 grm. charges of ore to ascertain the conditions under which a high extraction of radium is obtained. These established the influence on the efficiency of the process of such factors as concentration of acid, temperature, period of digestion, fineness of division of the ore, and grade of ore. The experiments were then extended to ore charges of a kilogrm., and later to ten kilogrms.

Inasmuch as the addition of water to a solution of barium bisulphate in concentrated sulphuric acid results in the partial precipitation of normal barium sulphate, it might be expected that treatment of the ore with acid somewhat diluted would materially reduce the percentage of radium extracted. By boiling 100 grm. charges of the low-grade ore for half an hour with acid containing respectively 96, 84, 78, 63, 49, and 35 per cent of H_2SO_4 corresponding extractions of 95, 93, 92, 78, 52, 42 per cent were obtained. It was thus established that digestion of the ore with crude sulphuric acid containing 78 or more per cent H_2SO_4 (60° Baumé acid or stronger) removes fully 90 per cent of the radium. Acid containing 35 per cent H_2SO_4 effectively removes the vanadium and uranium from the ore, leaving a light grey sandy residue.

The temperature of digestion appears to be of less influence than the concentration of acid employed. For example, an extraction of 84 per cent was obtained by treating the low-grade ore with 90 per cent acid at room temperatures, but the digestion period was extended to twenty-four hours.

Working with low-grade ore it was found that the period of digestion could be reduced to fifteen minutes by adding the ore to boiling concentrated acid and stirring the mixture vigorously. The extractions exceeded 90 per cent whenever 60° Baumé acid or stronger was employed. The decomposition of the high-grade ore with hot concentrated acid progressed more slowly. Boiling the ore sample with 90 per cent acid for an hour and until a temperature of 290° was reached resulted in an extraction of 89 per cent of the radium. The sandy residue after drying still retained a faint yellow colour, characteristic of very low-grade carnotites. By extending the digestion period to three hours an extraction of 92 per cent was finally obtained.

With ore coarser than 20-mesh the acid fails to penetrate the larger grains fully. An experiment with low-grade ore sized to pass through a 10-mesh sieve and held by 20 mesh resulted in an extraction of only 74 per cent of radium when boiled with 85 per cent acid for half an hour.

In the experiments with larger quantities of ore the digestions were conducted mainly with the crude acid known commercially as 60° Baumé, which contains approximately 78 per cent of H_2SO_4.

A brief description of a typical experiment will illustrate the process. Eighteen litres of 60° acid are heated to 190° in a cast-iron kettle of 50 litres' capacity. Ten kilogrms. of the low-grade ore, ground to pass a 20-mesh sieve, are then gradually added to the hot acid, with occasional stirring of the mixture with an iron ladle. A vigorous interaction occurs, accompanied by considerable frothing and evolution of carbon dioxide. The hot acid converts the uranium, vanadium, and some of the iron and aluminium constituents of the ore into water-soluble compounds. Calcium, barium, and radium are converted to bisulphates, which remain in solution in excess of hot acid. The sands, consisting of silica and silicates, are not materially acted upon by the hot acid and so remain as an insoluble residue.

The ore is boiled with the acid at least fifteen minutes and until the temperature rises to approximately 220°. When the contents of the kettle have cooled to 130° the material is transferred to a stoneware suction filter, previously heated to 100° by steaming it for an hour to prevent cracking of the heavy walls when the hot ore and acid mixture is dumped on the filter. A circular suction filter 40 cm. in diameter, with a capacity of about 30 litres in each compartment, when fitted with a "Filtros" filter serves admirably for separation of the acid from the ore residue. ("Filtros" is a mineral filtering medium unaffected by hot concentrated sulphuric acid. It is produced by the General Filtration Company, of Rochester, N.Y. Grades 7-R and 5—3, 4 cm. thick, were used). By spreading the coarse portion of the ore residue on the filter first the fine particles in the supernatant liquor do not clog up the filter, and filtration under a diminished pressure of 5 to 10 cm. of mercury is then quite rapid. In less than half an hour the residue on the filter is dry, and nearly 10 litres of clear acid liquor have been separated. The ore residue is then washed by stirring it up thoroughly on the filter with 5 litres of hot concentrated acid. After separation of the first wash acid the ore residue is given a second washing with 5 litres of hot acid. It is desirable to conduct the filtrations while the acid is hot, to avoid the separation of crystals of acid sulphates of iron, uranium, and vanadium, which are slowly deposited when the acid liquors attain room temperatures.

From the combined acid liquors, amounting to nearly 20 litres, the radium is recovered by pouring the acid into fully eight times its volume of hot water contained in a wooden or stoneware tank. Ordinary tap water may be used for diluting the acid. The resulting green solution contains a portion of the vanadium and uranium compounds. It should be well stirred to promote the solution of calcium sulphate. The ore contains sufficient barium compounds for the precipitation of the radium as radium-barium sulphate. The recovery of radium is, however, increased nearly 2 per cent by diluting with water containing a small quantity of some soluble barium salt. In most of the experiments water containing 5 grms. of barium chloride per 100 litres was used.

After standing at least three days to complete the precipitation of the radium-barium sulphates the supernatant liquor is syphoned off, the precipitate of sulphates is collected on a filter, washed twice with hot water containing a trace of barium chloride, and is then dried. The crude

TABLE II.—*Experimental Data.*

No.	Datum.	Low-grade ore.	Low-grade ore.	High-grade ore.	High-grade ore.
1.	Ore charge	1 kilogrm.	10 kilogrms.	1 kilogrm.	3 × 1 kilogrm.
2.	Ore residue (tailings).. ..	808 kilogrms.	8·22 kilogrms.	585 grms.	2497 grms.
3.	Soluble portion	19·2 per cent	17·8 per cent	41·5 per cent	16·8 per cent
4.	Acid used for digestion ..	1·8 l., sp. gr. 1·81	18 l., sp. gr. 1·72	20 l., sp. gr. 1·82	3·4 l., sp. gr. 1·81
5.	Wash acid used	1·1 l., sp. gr. 1·81	10 l., sp. gr. 1·72	1·1 l., sp. gr. 1·82	
6.	Final temperature	250°	210°	285°	270°
7.	Digestion periods	1 hour	15 min.	30 min.	20 min. each
8.	Acid sulphates	3·697 grms.	34·88 grms.	15·33 grms.	9·33 grms.
9.	Water sulphates..	1·754 grms.	32·5 grms.	3·22 grms.	8·57 grms.
10	Radium in acid sulphates..	$4{\cdot}28 \times 10^{-6}$ grms.	$39{\cdot}28 \times 10^{-6}$ grms.	$35{\cdot}59 \times 10^{-6}$ grms.	$11{\cdot}64 \times 10^{-6}$ grms.
11.	Radium in water sulphates	$0{\cdot}29 \times 10^{-6}$ grms.	$4{\cdot}25 \times 10^{-6}$ grms.	$1{\cdot}37 \times 10^{-6}$ grms.	$0{\cdot}97 \times 10^{-6}$ grms.
12.	Total radium recovered ..	$4{\cdot}57 \times 10^{-6}$ grms.	$43{\cdot}53 \times 10^{-6}$ grms.	$36{\cdot}96 \times 10^{-6}$ grms.	$12{\cdot}61 \times 10^{-6}$ grms.
13.	Total radium in ore	$4{\cdot}88 \times 10^{-6}$ grms.	$48{\cdot}80 \times 10^{-6}$ grms.	$42{\cdot}78 \times 10^{-6}$ grms.	$14{\cdot}64 \times 10^{-6}$ grms.
14.	Radium recovered	93·6 per cent	89·2 per cent	86·4 per cent	86.1 per cent
15.	Radium in acid sulphates..	87·7 "	80·5 "	83·2 "	79·5 "
16.	Radium in water sulphates	5·9 "	8·7 "	3·2 "	6.6 "
17.	Radium in acid liquors ..	$18{\cdot}2 \times 10^{-9}$ grms.	$20{\cdot}5 \times 10^{-8}$ grms.	—	—
18.	Radium in wash water ..	$10{\cdot}1 \times 10^{-9}$ grms.	$9{\cdot}5 \times 10^{-8}$ grms.	—	—
19.	Total radium in liquors (17 and 18)	$28{\cdot}3 \times 10^{-9}$ grms.	$30{\cdot}0 \times 10^{-8}$ grms.	$2{\cdot}22 \times 10^{-8}$ grms.	$10{\cdot}39 \times 10^{-8}$ grms.
20.	Radium loss in liquors ..	0·58 per cent	0·61 per cent	0·52 per cent	0·71 per cent
21.	Ra left in ore residue.. ..	$3{\cdot}52 \times 10^{-7}$ grms.	$4{\cdot}0 \times 10^{-6}$ grms.	$2{\cdot}62 \times 10^{-6}$ grms.	18×10^{-7} grms.
22.	Ra in ore residue	7·2 per cent	8·2 per cent	10·8 per cent	12·3 per cent
23.	Ra loss (20 + 22)..	7·78 "	8·81 "	11·32 "	12·91 "
24.	Recovery based on losses..	92·2 "	91·2 "	88.7 "	87·2 "
25.	Actual recovery	93·6 "	89·2 "	86·4 "	86·1 "
26.	Difference	+1·4 "	−2·0 "	−2·3 "	−1·1 "

sulphates thus obtained are designated *acid* sulphates in Table II.

The residue on the filter contains a portion of the vanadium, uranium, and iron sulphates, which are readily soluble in water. The acid in the residue also retains some radium. By washing the residue several times with hot water on the filter, with thorough stirring, a nearly white sand remains, which is covered with a thin layer of drab-coloured clay. The deep blue filtrate, however, is always slightly turbid, and upon standing a white precipitate settles out, which contains 3 to 9 per cent of the radium recovered. The precipitate consists largely of finely divided silica and silicates, but also contains a small quantity of radium-barium sulphate, which is precipitated in such finely divided form when the ore residue is leached with water as to pass through the filter. This radio-active precipitate is designated *water* sulphates.

The experiments with 1 kilogrm. lots of ore were conducted with similar apparatus of very much smaller dimensions. The filtrations were made with a large filter flask and Büchner funnel fitted with a "Filtros" filter, and extended in height by means of a cylinder of copper. Asbestos fibre was used as a packing material. The cast-iron kettle of the smaller unit is still in service, after having been used in at least forty extractions, and in a few experiments boiling was continued three hours. The record of the larger kettle is less gratifying: in the fifth run acid trickled out at two places, evidently due to blow-holes in the casting. Repairs were made with iron plugs, which have not required further attention in four subsequent runs.

Instead of recovering the radium from the concentrated acid liquor separated after treatment of one charge of ore this liquor may be used for the extraction of radium from a second and even a third charge of ore before the radium is recovered by dilution of the acid liquor with water. By treating several charges of ore with the same acid its radium content is correspondingly increased and some saving in acid is effected. The radium extraction, however, is thereby decreased to some extent, as shown by the data in the last column of Table II.

Some typical experimental data are also given. Items 17 and 18 have reference to the radium remaining in solution after dilution of the strong acid liquors.

The concentration of radium in the crude sulphates precipitated from the acid liquor varied somewhat in different experiments with the same grade of ore. The acid sulphates obtained from the low-grade ore averaged $1{\cdot}15 \times 10^{-6}$ grm. radium per grm.—*i.e.*, 1150 parts per billion. A comparison with the radium content of the ore, $4{\cdot}88 \times 10^{-9}$ grm. radium per grm., shows that the concentration of radium has been increased approximately 235 times. The acid sulphates from the high-grade ore, on the other hand, contained $2{\cdot}32 \times 10^{-6}$ grm. radium per grm., a concentration double that of the sulphates separated from the low-grade ore, but the concentration ratio of radium in sulphate to radium in ore is only 55.

It is seen that less than 1 per cent radium remains in solution in the combined solutions after dilution. However, it should be stated that values as high as 5 per cent were obtained in some experiments when the solutions were filtered off after standing for only six to ten hours. The low values represent the quantities remaining in solution after a period of at least three days.

Although more radium was actually recovered in a few experiments than was to be expected on the basis of the combined radium losses in tailings and solutions, in general the recovery fell short from 2 to 5 per cent. I am inclined to ascribe this loss largely to retention of radium-barium sulphate in the thick filter plate. Likewise the quantities of insoluble material that appear in the filtrate when the ore residue is leached with water depend primarily upon the porosity of the "Filtros" filter used.

The sediment that appears in the water filtrate consists largely of finely divided silicates. A qualitative examination showed the presence of aluminium, calcium, magnesium, and much silica. The sulphates of the alkaline earths constitute a relatively small proportion of the sediment.

The acid sulphates even after ignition are not pure white but retain a grey colour. The acid sulphates separated from three kilogrms. of low-grade ore were found to contain 6·63 per cent of lead sulphate, 3·83 per cent of ron and aluminium weighed as oxides, and 2·27 per cent of silica. The relatively high percentage of lead sulphate is largely introduced with the crude acid used in treatment of the ore. Barium of course predominates in the sulphates of the alkaline earths, but calcium and strontium are also present.

We realise that this investigation is incomplete in several respects. It should be extended to carnotites from other localities and to ores of different composition. The recovery of acid from the liquors and the separation of uranium and vanadium from the solutions have been given but scant attention. The distribution and recovery of the other radio-active constituents of the ore would be of interest. More important, however, would be a comparative study of methods to ascertain the industrial possibilities of this method of extraction.

Preliminary experiments conducted with samarskite indicate that fully 70 per cent of the radium of the mineral can be extracted by treatment with concentrated sulphuric acid.—*Journal of Physical Chemistry*, 1916, xx., No. 6, 485.

PURE SODIUM CHLORIDE.

By CLIFFORD LOHMAN.

It is often convenient and necessary to have a supply of pure sodium chloride for the preparation of standard solutions. It is quite an easy matter to obtain the substance with a "C.P." label, but it does not always follow that the article is as pure as the label may indicate.

It seems to be a difficult matter to obtain common salt that is entirely free from potassium chloride. We have prepared sodium chloride by different methods, and have tested these and also the different samples we had on hand in the laboratory stock room, and have usually found small quantity of potassium chloride present.

1. We prepared a saturated solution of ordinary common salt into which we passed hydrogen chloride, made by heating pure concentrated hydrochloric acid. We filtered off the salt crystals, using a pump, and after drying we obtained 0·42 per cent of potassium chloride.

2. We dissolved 100 grms. of ordinary common salt in 300 cc. water, and filtered into an evaporating dish. This was heated to boiling, and milk of lime added in small excess. The precipitate was filtered off, and the excess of calcium and barium precipitated with sodium carbonate. It was again filtered, and the excess of sodium carbonate was changed to sodium chloride with dilute hydrochloric acid. After drying we found in the specimen 0·32 per cent of potassium chloride.

3. We made a solution of caustic soda by dissolving metallic sodium in distilled water, and neutralised this with hydrochloric acid. The analysis of the dried salt showed 0·27 per cent of potassium chloride. The sodium must have contained a small quantity of metallic potassium.

4. The foregoing experiment was repeated, using the purest caustic soda in the laboratory, that had not been purified by alcohol. The resulting sodium chloride showed 0·48 per cent potassium chloride.

We next examined three specimens of sodium chloride, each of which was supposed to be chemically pure. The following results in potassium chloride were obtained:—

1. 0·57 per cent.
2. 0·45 per cent.
3. 0·49 per cent.

In each of the seven samples of salt examined the presence of the potassium could be distinctly seen with the flame test, using a piece of blue glass.

The method employed in separating the sodium and potassium chlorides is the following:—We dissolved about a half grm. of the salt in a little water, and added perhaps twenty drops of a 10 per cent solution of platinic chloride. Then we added a few drops of water, and moved the mass back and forth until it flowed freely. There is some difficulty of manipulation here, as too little water would not dissolve all the Na_2PtCl_6 and too much would dissolve some K_2PtCl_6. We filtered and washed first, five or six times with one volume of water and a half volume of alcohol, then about six times with a mixture of alcohol and ether. After drying the precipitate it was placed over a weighed platinum crucible and washed into the crucible with boiling water.

We desire to express our thanks to Dr. N. Knight for the aid he rendered in this work.

Cornell College, July 4, 1916.

SEPARATION OF THE METALS OF THE TIN GROUP.*

By J. M. WELCH and H. C. P. WEBER.

The customary methods for the separation of arsenic, antimony, and tin for qualitative purposes depend in principle either on the relative strength of the acids of these elements (for instance, the ammonium carbonate separation of arsenic from antimony and tin) or upon the difference in the solubilities of their sulphides in acids. (A separation based upon the precipitation of antimony as the pyroantimonate of sodium has been proposed by Hahn, *Zeit. Anorg. Chem.*, 1915, xcii., 168). Of these principles the latter is perhaps the one most made use of in present practice.

Thus in the procedure outlined by A. A. Noyes and W. Bray (*Journ. Am. Chem. Soc.*, 1907, xxix., 137) the three elements are separated from each other by the use of graded concentrations of hydrochloric acid. In the hands of a practiced operator this method leaves little to be desired and is one of the most satisfactory methods described. When, however, the method was employed by persons of less manipulative expertness, such as students entering for the first time into qualitative work, the results were by no means as satisfactory as might have been anticipated. The statistics collected show tin as giving the greatest trouble, it being missed in 20·2 per cent of the cases considered. (From reports of the students in qualitative analysis, first semester 1914—1915; about 200 reports were examined). Arsenic was overlooked in 18 per cent of the cases, while antimony was very rarely missed (less than 1 per cent).

According to the method of Noyes the sulphides of the second group are precipitated and then separated by treatment with ammonium polysulphide in much the usual manner, As_2S_5, Sb_2S_5, and SnS_2 being thrown out from the resulting polysulphide filtrate upon acidification with hydrochloric acid. Up to this point no particular difficulty is encountered, except occasionally with copper, which dissolves to a slight extent in ammonium polysulphide. This will be referred to again under the description of the new procedure.

The precipitated tin group sulphides, superficially dried, are then treated with exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1·2) and warmed for ten minutes on the steam bath. Arsenic sulphide remains behind, and antimony and tin go into solution as $SbCl_3$ and $SnCl_4$ respectively.

Up to this point the method here proposed follows the lines laid out by Noyes and Bray (*loc. cit.*), but from here on the procedure is modified. In the original method the filtrate containing the antimony and tin is diluted so that 50 cc. of solution contain 10 cc. of concentrated hydrochloric acid. Hydrogen sulphide is then passed into the solution, *which meanwhile should be kept at* 90°. If no precipitate is formed, further 5 cc. of water are added and hydrogen sulphide is again passed into the solution. If antimony sulphide has been formed it is removed by filtration, the tin is then precipitated as the sulphide from the cold solution after dilution to 70 cc.

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* Presented as Thesis for the Degree of B.S. by J. M. Welch to the College of Liberal Arts and Sciences, University of Illinois. From the *Journal of the American Chemical Society*, xxxviii., No. 5.

If these steps are carried out with proper attention to the essential details the results are very satisfactory. The limits of dilution are not very wide, however, and in addition the temperature must be controlled. Errors at this point of the procedure will cause the formation of a "brown precipitate," as has been noted by Noyes and Bray. As a matter of experience this error was a very common one on the part of numerous students using the method. Aside from the fact that the characteristic colour of antimony sulphide is masked, producing corresponding uncertainty in the interpretation of the results, large quantities of tin are lost with the antimony. Unless the precipitate is again treated by a special procedure tin may be and often is overlooked entirely.

Experimental.

In the literature very little is to be found concerning the nature of the brown precipitate formed when antimony and tin sulphides are precipitated together. Its colour in no way corresponds to that of a mixture of the two sulphides, and in view of the regularity and ease with which it is formed it is strange that so little mention is made of it. Of the well-known texts on qualitative analysis, that of A. A. Noyes and one or two others are the only ones which mention it. No reference is found in the general literature. Pouget has described a number of compounds which are possibly of the same nature (*Comptes Rendus*, 1897, cxxiv., 1445, 1518; 1898, cxxvi., 1144, 1792; 1898, cxxix., 103). By precipitating salts of the metals with solutions containing K_3SbS_3 he obtained compounds of the type Me_3SbS_3 and Me_2KSbS_3. For the heavy metals these are brown to black precipitates of constant composition. The alkali-earth compounds are white to yellow, the manganese salt is rose-coloured. The mineral pyrargyrite, Ag_3SbS_3, is a naturally occurring example of these thioantimonites. The tin thioantimonite has not been described.

It is possible that the brown precipitate is of the same general character as the compounds described by Pouget. It is formed whenever tin and antimony sulphides are precipitated together from a dilute hydrochloric acid solution. When equivalent portions of nearly neutral solutions of sodium thioantimonite and stannic chloride are mixed (molar solutions) a muddy black precipitate is formed at once, which darkens on standing. With excess of antimony the colour is shifted somewhat to the red, while with corresponding excess of tin the yellow predominates more and more. Occasionally, when much antimony is present, its sulphide may be observed to form first on passing hydrogen sulphide into the solution, and as the precipitation proceeds the characteristic drab-coloured compound is formed. The preparation of a definite tin thioantimonite has so far not been undertaken, but the characteristic way in which such solutions reacted led to an investigation of the reliability of the behaviour as an indication of tin and antimony.

In order to determine the limits between which this substance would reveal its presence varying quantities of stannic tin and trivalent antimony were mixed and diluted to 70 cc., with an acid content of 10 cc. of hydrochloric acid. These solutions were then precipitated at ordinary temperatures by means of hydrogen sulphide. The relative concentrations of the two metals in the test solutions are given in Table I.

Solutions "A" to "K" gave red to red-brown precipitates, "K" to "S" were decidedly brown, while the precipitates from solutions "R" to "Y" varied from clay-brown to yellow-brown.

With the ratio of the antimony content to the tin content varying as given in solutions "I" to "U" the brown colour was easily recognised, being most sharply defined in the region indicated by solutions "K" to "S" inclusive. When the antimony was present in greater proportion than is indicated in "I," it was difficult to discover a marked difference between the colour of the precipitate and that of a precipitate of antimony sulphide alone. When the proportion of the tin exceeded that given in solution "U" the yellow colour of tin sulphide predominated, so that there could be no doubt as to its presence. The presence of antimony was indicated under these conditions by the red precipitate first formed when hydrogen sulphide was passed into the solution.

Table I.—*Composition of Solutions for the Investigation of the "Brown Precipitate."*

Solution.	Sb per cc. (mgrm.).	Sn per cc. (mgrm.).	Ratio Sb/Sn.
A	6·30	0·32	20/1
B	5·98	0·32	19/1
C	5·66	0·32	18/1
D	5·34	0·32	17/1
E	5·02	0·32	16/1
F	4·70	0·32	15/1
G	4·38	0·32	14/1
H	4·06	0·32	13/1
I	3·74	0·32	12/1
J	3·52	0·32	11/1
K	3·20	0·32	10/1
L	2·88	0·64	9/2
M	2·56	0·96	8/3
N	2·24	1·28	7/4
O	1·92	1·60	6/5
P	1·60	1·92	5/6
Q	1·28	2·24	4/7
R	0·96	2·56	3/8
S	0·64	2·88	2/9
T	0·32	3·20	1/10
U	0·32	3·52	1/11
V	0·32	3·74	1/12
W	0·32	4·06	1/13
X	0·32	4·38	1/14
Y	0·32	4·70	1/15

It was found that within the limits indicated not only was the characteristic brown precipitate obtained, but also that a colorimetric estimate of the relative proportions of the two constituents, tin and antimony, was possible. In order to show this the precipitates listed in Table I. were renumbered, so as not to suggest their composition, and beginners from the laboratory were asked to arrange them in the order of the colour gradations from red through brown to yellow. This was repeated a number of times, and in every case the precipitates from "K" to "S" inclusive were arranged in the order of decreasing antimony-tin ratio.

From this it would appear that when the ratio of antimony and tin in a mixture lies between 12/1 and 1/12 the colour of the precipitate formed by the action of hydrogen sulphide in a solution containing the equivalent of 10 cc. of concentrated hydrochloric acid to a volume of 70 cc. is a very valuable indication of the presence of tin.

Treatment of the Precipitate.—If a separation of the antimony and tin is not desired the precipitate is ready for the procedure devised by Pertusi and Gastaldi (*Rend. Soc. Chim. Ital.*, 1914, iv., 83). According to this method the sulphides are suspended in a little water and shaken with metallic magnesium powder. The tin compound is reduced to the metal and is after reduction dissolved in dilute hydrochloric acid. The solution is allowed to run through a filter into mercuric chloride solution, the $SnCl_2$ revealing its presence by the production of mercurous chloride. The antimony does not interfere with the reaction, and in the case of all mixtures listed in Table I. satisfactory tests were obtained for tin by this method. No particular account is taken of antimony in this process, however, and it seemed advisable to include a positive confirmation of this element in the steps taken, particularly to take care of the extreme mixtures where antimony or tin predominates very largely.

One of the most satisfactory tin and antimony separations is that of F. W. Clarke (CHEMICAL NEWS, 1870, xxi., 124), which is used for the quantitative separation of these two elements. A series of tests of this method was made for the purpose directly in view, with solutions similar to those given in Table I. In these the proportion of antimony to tin ranged from 20/1 to 1/20, and in every instance both elements were recognised without difficulty. The conditions of the separation are that the combined weight of the two metals shall not exceed 0·3 grm., that for each 0·1 grm. there should be present 5 grms. of oxalic acid, and that the tin should be in the stannic form. These conditions are readily met in the ordinary qualitative separation.

In the separation as ordinarily carried out H_2S is passed into the hot oxalic acid solution. Antimony sulphide precipitates, of characteristic colour and easily filtered, and tin remains in solution. A reversal of the steps was examined for its usefulness, but was found unsatisfactory. It is not possible to achieve a sharp separation of antimony and tin by boiling the mixed sulphides with an oxalic acid solution. Either the tin does not completely dissolve or some of the antimony dissolves with it. It was therefore found necessary to dissolve the antimony-tin mixture completely and then to precipitate the antimony alone. The steps as finally devised will be described under the procedure.

Procedure.

To the precipitated sulphides from ammonium sulphide separation, after having dried them superficially either by suction or by pressing between filter paper, add exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1·20) and heat for ten minutes on the steam bath. Arsenic sulphide remains behind and is removed by filtration and examined in the customary manner.

It is assumed that the ammonium sulphide separation from the copper group has been sharp and that neither mercury nor copper is present in this portion of the material. It often occurs that copper dissolves in the ammonium polysulphide (which shows itself in the brown colour of the solution). Sodium sulphide does not present this difficulty, but it dissolves mercuric sulphide. If ammonium polysulphide, to which about 5 per cent of NaOH has been added, is used, both difficulties are avoided and a reagent of striking superiority over ammonium polysulphide alone is obtained. To show this the following mixtures were precipitated: Two test-tubes, each with mgrm.-mols. of mercury, tin, and antimony; two, each with mgrm.-mols. of copper, antimony, and tin. The precipitates were washed by decantation, and to one of the mercury precipitates and to one of the copper precipitates ammonium polysulphide, containing 5 per cent of NaOH, was added. To the other two precipitates ammonium polysulphide without NaOH was added. All four test-tubes were placed in boiling water. The tin group sulphides dissolved immediately in the solvents containing NaOH, and in three minutes the contents of the two tubes consisted of a clear golden-yellow solution free from copper or mercury, and a jet-black, dense precipitate of the copper group sulphide at the bottom of the tube. In the comparison tubes, on the other hand, the tin group had not under the same conditions dissolved completely after three hours, and, furthermore, the ammonium polysulphide had disolved an appreciable amount of *copper*.

The filtrate from the arsenic, which contains antimony trichloride and tin tetrachloride, is diluted to a volume of 70 cc. and is saturated with H_2S. If the addition of the H_2S takes place while the solution is hot a portion of the antimony will precipitate first as the red sulphide, but on further addition of H_2S, and as the solution cools, a brown to nearly black precipitate is formed, which is characteristic of tin plus antimony. With practice the intensity of the coloration may be made the basis of an estimate of the relative quantities of the two constituents. As soon as the formation of this precipitate is observed the introduction of H_2S is interrupted and the solution and precipitate are heated again until the excess of H_2S is driven off. Five cc. of hydrogen peroxide solution (3 per cent) are added and the solution is heated until the precipitate has redissolved. Five to 10 grms. of oxalic acid are now added and H_2S is again passed into the hot solution, which is allowed to cool while it is being saturated. Antimony sulphide precipitates as a bright red, easily filtered precipitate, and is then collected on the filter.

The mixed precipitate may be redissolved by simply evaporating the solution with the precipitate. Upon addition of H_2O_2 the same end is attained without evaporation and in much shorter time. A few drops of bromine water are still more effective in this respect. The excess H_2S is best driven off before adding these oxidising agents. A large excess should of course not be used, since it would decompose the oxalic acid added later. As antimony sulphide is to be precipitated at the next step it is not necessary to wait for the last faint red cloud of antimony sulphide to redissolve at this part of the procedure.

The filtrate from the antimony sulphide, which contains the tin, or a portion of the filtrate (10 cc. is usually sufficient), is boiled with 1—2 grm. of granulated test lead for two or three minutes. The solution is then chilled (by running water) and filtered into a solution of mercuric chloride. In the presence of tin white mercurous chloride is formed.

The solution contains tin in the tetravalent state. Upon boiling this with metallic lead it is reduced to stannous tin, which gives the well-known reaction with mercuric chloride. Trials in connection with the method showed that it was reliable with as little as 0·5 mgrm. of tin. Some of the lead goes into solution during the heating and crystallises out again upon cooling (as lead chloride). While this precipitate is different in character from the mercurous chloride errors are avoided by cooling the solution first and filtering from the lead salt.

Summary.

1. It has been shown that when antimony and tin are precipitated together as sulphides they form a characteristic brown precipitate (which is possibly a sulphantimonite of tin). Within rather wide limits this is a reliable indication of the presence of these two elements.

2. It was found that the reduction of stannic compounds to stannous compounds by means of metallic lead could be carried out with sufficient ease and accuracy to make it available as a method for the detection of tin.

3. A method for the qualitative analysis of the tin group has been described, which has proven effective in use, particularly in the hands of inexperienced students, and which it is believed has some advantages in latitude of conditions, speed, and ease of manipulation.

THE DETERMINATION OF METHYL AND ETHYL ALCOHOL IN SPIRIT VARNISHES.*

By G. W. KNIGHT and C. T. LINCOLN.

IN the analysis of spirit varnishes for methyl and ethyl alcohol, the analyst is confronted with the problem of determining these constituents in the presence of other organic solvents which are difficult to separate from the alcohols. Chief among these are acetone and other ketones, and pyridine. Although pyridine seldom occurs in large quantity in commercial spirit varnishes, it is sometimes used in the denaturing of grain alcohol, and consequently enters into the ultimate composition of varnishes which are made from denatured alcohol. Crude acetone, however, is frequently used in considerable amounts both alone and as a constituent of crude wood spirits; so any method to be practicable would have to give accurate results in the presence of these substances.

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* Contributed with the permission of the Secretary of the Treasury and the U.S Appraiser, Port of New York. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 10.

Determination of Ethyl Alcohol.

For the determination of ethyl alcohol in varnishes containing volatile organic substances slightly soluble in saturated salt water solution, but soluble in petroleum ether, the method of Thorpe and Holmes gives very satisfactory results (*Trans. Chem. Soc.*, 1903, lxxxiii., 314). In the presence of acetone and other substances which are miscible in all proportions with water, however, the method is capable of giving very misleading results. As may be seen from theoretical considerations, and as has been actually shown in the practical working of the method in these cases, a number of extractions with the immiscible solvent directly proportional to the percentage of acetone present in the water solution, and inversely proportional to the ratio of the volume of the petroleum ether to that of the water solution, are necessary to reduce the amount of acetone in the final distillate to a negligible quantity. By the time this is accomplished an appreciable quantity of alcohol has been lost.

The most satisfactory method for determining ethyl alcohol, in the absence of methyl alcohol, and in the presence of appreciable quantities of acetone and similar substances, is to treat the alcohol, which is first distilled to separate it from most of the other constituents of the varnish, with phosphorus and iodine, forming ethyl iodide; and the ethyl alcohol present may then be calculated from the amount of ethyl iodide formed as described later on.

Determination of Methyl Alcohol.

Where "Columbian spirits" have been used in the preparation of the varnish and no appreciable amount of acetone or ethyl alcohol is present, ordinary distillation conducted in such a way as to have not more than 25 per cent of alcohol in the final distillate, and consequent calculation of the percentage by means of the specific gravity tables of Klason and Norlin (combined with the Thorpe and Holmes method, where necessary), gives very satisfactory results (*Arkiv. Kem. Min. Geol.*, 1907, ii., 27).

In the presence of acetone and the absence of ethyl alcohol the method used for determining ethyl alcohol under similar conditions, as previously described, gives the best results.

Determination of Mixtures of Ethyl and Methyl Alcohol—Acetone Absent.

The method devised by Leach and Lythgoe is generally recommended in standard works for the determination of methyl and ethyl alcohol in tinctures and essences (*Journ. Am. Chem. Soc.*, 1905, xxvii., 964).

A few years ago one of the writers had occasion to analyse many hair tonics and similar preparations for methyl and ethyl alcohol. After the preparations had been analysed, the method was tested with solutions containing similar quantities of the alcohols to those found. The results were far from satisfactory, An investigation into the cause of the inaccuracy led to the discovery that the assumption on which part of the method is based; *i.e.*, that the specific gravity of solutions of methyl alcohol in water is the same as that of ethyl alcohol for the same percentages of the alcohol by weight in the solution, is correct only for certain concentrations. The tables of Klason and Norlin for methyl alcohol and those in *Bull.* 107 (Rev.) of the Bureau of Chemistry both calculated for about the same temperatures (60° F./60° F. and 15° C./15° C.) are practically identical for dilutions of from 0 to 7 per cent of the alcohol by weight. From 7 per cent up, however, there is a gradually increasing difference until at 25 per cent by weight there is a difference of over 2 per cent. Consequently, the error in the Leach and Lythgoe method increases in proportion as the ratio of methyl alcohol to total alcohol increases, and also in proportion to the percentage of total alcohol in the preparation; the maximum error occurs in the case where the substance analysed contains nearly 100 per cent of total alcohol, and the percentage of ethyl alcohol present is very small. This happened to be the case in the experience mentioned by the writers. The hair tonics contained over 90 per cent of total alcohol and less than 10 per cent of ethyl alcohol, and the error introduced by the Leach and Lythgoe method amounted to about 8 per cent.

To obtain accurate results by this method it is necessary to modify the process of calculating and using the tables. The following example, the same as that given by Leach and Lythgoe (*loc. cit.*) to show the method of calculating percentages of the alcohols from the specific gravity and refractometer reading, will illustrate the difference in the results obtained by their process of calculation and the modified one.

Assuming that 25 cc. of the varnish had been diluted to 125 cc. and 100 cc. of distillate collected after purifying by the Thorpe and Holmes process, that the specific gravity of the distillate at 15·6° C./15·6° C. was 0·9735, and the refractometer reading at 20° C. was 35·8, then the Leach and Lythgoe method would give:—

38·48 per cent CH_3OH by weight
35·04 per cent C_2H_5OH by weight

73·52 per cent total alcohol by weight

Using the same data and the modified method of calculation the following results would be obtained:—

32·80 per cent CH_3OH by weight
37·08 per cent C_7H_5OH by weight

69·88 per cent total alcohol by weight

or a difference of:—

+5·68 per cent CH_3OH by weight
−2·04 per cent C_2H_5OH by weight

+3·64 per cent total alcohol by weight.

Thus to obtain results of reasonable accuracy by the use of the Leach and Lythgoe method, the calculation of results must be conducted in the following manner in every case where the per cent of total alcohol in the final distillate falls between 8 per cent and 40 per cent of total alcohol by volume, and an appreciable amount of methyl alcohol is present. Known mixtures of methyl and ethyl alcohol have been analysed by the writers, using this modified method of calculation, with satisfactory results. The same example as that given above will serve to show the details of the calculation.

The specific gravity of the distillate 0·97350 corresponds to 18·38 per cent ethyl alcohol by weight and 16·43 per cent methyl alcohol by weight. The refractometer reading, 35·8 at 20° C., corresponds to 52·3 per cent of methyl alcohol on total alcohol, using the figure 18·38 as the per cent of total alcohol tentatively. Multiplying 523 by (18·38 − 16·43) and subtracting the product (1·02) from 18·38 gives 17·36, the approximate per cent of total alcohols by weight. By using this figure now instead of 18·38 to obtain the ratio of methyl alcohol to total alcohol by use of the refractometer reading and tables, 46·1 per cent of methyl alcohol is obtained. Re-calculating the percentage of total alcohol now with this new percentage of methyl alcohol, 17·48 per cent is obtained. Repeating the calculation 17·47 is obtained as the true per cent of total alcohols, and 46·9 as the true per cent of methyl alcohol of total alcohols, in place of 18·38 and 52·3 per cent, respectively.

The oxidation method of Thorpe and Holmes may also be used in the absence of substances oxidisable to CO_2 by potassium bichromate and dilute sulphuric acid (1 : 4) (*Transactions Chem. Soc.*, 1904, lxxxv., 1). In this method methyl alcohol is wholly oxidised to CO_2 and H_2O, while ethyl alcohol is converted mostly to acetic acid, 0·5 per cent only being converted to CO_2. The CO_2 given off is collected in a soda-lime tube and weighed, correction being made for the CO_2 formed from any ethyl alcohol that may be present.

Determination of Mixtures of Ethyl and Methyl Alcohol—Acetone Present.

Spirit varnishes or other preparations containing appreciable quantities of acetone cannot be analysed for methyl and ethyl alcohol by either of the above methods with any degree of accuracy. One of the writers has obtained good results by precipitating out the acetone in the cold as iodoform with nascent iodine under conditions similar to those used in the Kebler method for the determination of acetone (*Journ. Am. Chem. Soc.*, April, 1897), shaking out the iodoform with chloroform and the traces of chloroform with petroleum ether, and then re-distilling a few times, and applying the modification of the Leach and Lythgoe method given above. But although the method gave good results when tried with known quantities of methyl alcohol, ethyl alcohol, and acetone, the manipulation was difficult and not easily mastered, the volumes of solutions were tedious, so that a more simple method was sought.

Of the many qualitative methods published, the oxidation method of Denigès (*Comptes Rendus*, 1910, cl., 832) recommended by Simmonds (*Analyst*, 1912, xxxvii., 16) for the quantitative determination of methyl alcohol in the presence of ethyl alcohol was thoroughly tried out, but it failed to give satisfactory or concordant results with known mixtures. This method, however, was found to be useful as a qualitative test to detect the possible presence of methyl alcohol in a distillate. Another test of Denigès is useful for the detection of ethyl alcohol in the presence of methyl alcohol (*Bull. Soc. Chim.*, 1910, vii., 951). In the former test the alcohols are oxidised to the corresponding aldehydes by $KMnO_4—H_2SO_4$ mixture, acetone not interfering with the test, and in the latter test the ethyl alcohol is oxidised to acetaldehyde with bromine water, the methyl alcohol not being appreciably affected. Schiff's reagent is used to detect the aldehyde formed, and in the first test enough H_2SO_4 is added to prevent the acetaldehyde formed from affecting the reagent. These tests have the fault inherent to all generic tests, in that they are unreliable in the presence of aldehydes or substances that oxidise to aldehydes when treated with these oxidising agents.

To obtain accurate results in the presence of acetone it is necessary to resort to a mode of procedure based on the formation of the alkyl iodides, and by analysing or determining certain physical constants, or further elaboration of these, obtain the amount of the alkyl radicle present. This is a more strictly chemical method than any of those mentioned heretofore, as the reactions are more specific in their nature; but the manipulation is difficult and tedious, and requires considerable skill and time.

Many methods depending on these reactions have been published, of which the prototype is the well-known qualitative method of Riche and Bardy for the detection of methyl alcohol in commercial spirit of wine (*Comptes Rendue*, 1875, lxxx., 1076).

Stritar and Zeidler form the iodides in the usual manner (*Zeit. Anal. Chem.*, 1904, xliii., 387), and then determine the quantity by making use of Zeisel's well-known method for the estimation of methoxy groups in which methyl iodide vapour is decomposed by an alcoholic silver nitrate solution and the silver iodide formed determined gravimetrically.

Kramer and Grodyki (Schmidt, *Lehrbuch der Pharm. Chem.*, 1901, ii., 191) determined the percentage of methyl alcohol in wood alcohol quantitatively by treating iodine and phosphorus with the wood alcohol, and a solution of iodine in hydriodic acid, distilling off the iodide, collecting the distillate in a measuring cylinder under water, and calculating the percentage of methyl alcohol from the volume of the iodide formed.

In the Krell method mentioned by Jones (*Allen's Com. Org. Anal.*, 1909, i., 91) as being used in a modified form in the British Government laboratory for estimating methyl alcohol in wood naphtha, the general outline of the method is very similar, but the addition of the solution of iodine in hydriodic acid is omitted, and the details of analysis are perfected. No other mention of this method was found in the literature.

Wirthle attempted to quantitatively determine methyl and ethyl alcohol in pure mixtures by the iodide method, but he was unable to obtain satisfactory results (*Zeit. Nahr. Genussm.*, 1912, xxxiv., 14). He fractionated and distilled the iodides and calculated the percentage of the alcohols from empirical figures. He also tried weighing the iodides, after purification, and then calculating the percentages of the alcohol from empirical figures. The saponification values of the iodides formed by him were determined, and the proper conditions for saponification studied.

Thorpe ("Dictionary of Applied Chemistry," 1912, i., 63) suggests the use of a method involving the distillation of the iodides similar to Wirthle's method, and gives a table showing the temperature at which the first drop distils over, and the volume distilling over below 72° C. from 10 cc. of mixed purified iodides, with corresponding percentages of methyl alcohol by volume in the mixture of alcohols for concentrations up to 10 per cent of methyl alcohol. He gives no detailed description of the apparatus used, nor the influence of barometric pressure on the boiling-point, but says that ethyl iodide has a constant boiling-point of 72° C. Thorpe also recommends the use of a modification of the Riche and Bardy method when the initial boiling-point is below 70° C., but merely for the qualitative detection of methyl alcohol. The final result is obtained by dyeing 2 to 3 feet of Berlin wool, using a smaller quantity of alcoholic solution of the oxidised aniline mixture than that recommended by Riche and Bardy, absolutely no colour being obtained in the absence of methyl alcohol.

Riche and Bardy, Kramer and Grodyki, Krell, Wirthle, and Thorpe all recommend different proportions of iodide and phosphorus to alcohol. Riche and Bardy used 15 grms. of iodine and 2 grms. of phosphorus to 10 cc. of alcohol, while Kramer and Grodyki used 15 grms. PI_3 and 5 cc. of a solution of 1 part I_2 in 1 part HI (sp. gr. 1·7) to 5 cc. alcohol. Krell adds his materials in the proportions of 44 grms. of iodine and 4 grms. of phosphorus to 10 cc. of alcohol. Wirthle, by calculation of the theoretical amount necessary, decides on about 32 grms. of iodine for each 10 cc. of methyl alcohol, and 22 grms. per each 10 cc. of ethyl alcohol, and in mixtures proportionate amounts. The amount of phosphorus necessary is calculated in the same manner. Thorpe recommends the use of 30 grms. of iodine and 2 grms. of phosphorus to 10 cc. of strong spirit.

Kramer and Grodyki, by their method of procedure, obtained a yield of about 92·5 per cent of the theoretical. They applied no external heat, and used a quantity of iodine largely in excess of the theoretical. Wirthle, using about the theoretical quantity of iodine necessary to carry on the reaction, got yields varying from 88·3 to 93·8 per cent for ethyl iodide, and from 89·2 to 90·5 per cent for methyl iodide. He heated the mixture of iodide, phosphorus, and alcohol on a water-bath under a reflux condenser, and regulated the heating so that the mixture would boil moderately. He was unable to account for the lack of uniformity in yields and consequent inaccuracy of results. The other investigators make no mention of yields.

Applying no external heat and using the quantity of iodine recommended by Thorpe for similar mixtures, we obtained yields of from 92·4 to 92·6 per cent for mixtures of the absolute alcohols containing from 1 up to 10 per cent of methyl alcohol. For pure methyl alcohol using the same procedure we obtained an 85 per cent yield. Working with a large excess of iodine and maintaining an external heat (75° C.), greatly in excess of the boiling-point of methyl iodide, as recommended in Krell's method, we obtained yields of 100 per cent with ethyl alcohol and 98 per cent with methyl alcohol. These results would seem to show that it is necessary to use a large excess of iodine and supply a considerable quantity of external heat for a long time to complete the reaction, and get a maximum or quantitative yield of the iodides. Either these iodides are endothermic compounds, or so large an amount of heat is taken out of the reaction mixture in the form of latent heat of vaporisation by the volatilisation of the easily volatile compounds composing the mixture that more heat must be supplied to complete the reaction. The slight loss we suffered in the case of methyl alcohol was undoubtedly due to solution of some of the methyl iodide in the 30 cc. of water under which it was collected. Methyl iodide is much more soluble in water than ethyl iodide. Rex gives the solubility in water at 20° C. of ethyl iodide as 0·40 grm. per 100 grms. of water, and of methyl iodide as 1·42 grms. per 100 grms. of water (*Zeit. Phys. Chem.*, lv., 355). Although under the conditions of the determination the water under which the iodides are collected is probably never saturated, their solubility in water is by no means a negligible factor in obtaining quantitative yields. The iodides seem to be as soluble in saturated salt solution as in water. To determine this point the writers saturated water first with methyl iodide and then with salt. No separation of iodine occurred. Evidently nothing can be gained by collecting the iodides under saturated salt solution, but the ratio of the volume of water coming in contact with the iodides before measuring them to the ultimate volume of the iodides should be as small as possible.

The conditions necessary for a maximum yield of the iodides having been determined, the next step was to ascertain the best mode of procedure for determining the percentages of methyl and ethyl iodide in the mixture, and ultimately the percentages of methyl and ethyl alcohol by volumes corresponding, preferably eliminating calculation from empirical figures if possible.

The method of determining the relative proportion of methyl and ethyl iodide in the mixture of iodides, suggested by Wirthle and worked out by Thorpe for mixtures containing 10 per cent and less of methyl iodide, was investigated. Wirthle gives the uncorrected boiling-point of ethyl iodide as 70·8° C., while Thorpe says it is always 72° C. Determining the boiling-point in the manner recommended by Mulliken ("Identification of Pure Organic Compounds," i., 221), the writers obtained in eight entirely different samples on different days uncorrected values of 71·7° C., 71·5° C., 71·6 C., 71·8° C., 71·5° C., 72·0° C., 71·4° C., 71·5° C., and a mean of 71·6°; the thermometer used was carefully standardised at this temperature, and found to be accurate. Corrected for stem exposure these values are 72·3° C., 71·2° C., 72·2° C., 72·4° C., 72·1° C., 72·6° C., 72·0° C., and 72·1° C., with an average of 72·1° C. The deviation from the mean in most cases was not more than 0·1° C., and was probably due to differences of barometric pressure, a difference of 10 mm. making a change of the boiling-point of about 0·4° C. Mixtures of methyl and ethyl iodide made from corresponding mixtures of ethyl and methyl alcohol containing up to 10 per cent of methyl alcohol were distilled with the same apparatus used above. As had been expected, different results were obtained from those found by Thorpe.

Mixtures of "Columbian spirits" with absolute ethyl alcohol and of wood spirits with absolute ethyl alcohol containing 9 per cent of absolute methyl alcohol of the total alcoholic contents were transformed into the corresponding iodides, and 10 cc. of the iodides distilled on the same day. The first drop distilled over at 62° C. in each case, and the volume of distillate received below 69° C. was the same in both cases, namely, 4·5 cc. The distillation was repeated in one case, and the distillation carried on more rapidly. In this case the first drop was collected at 61° C., showing the need of uniformity of distillation to obtain comparable results.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 30, 1916.

Prof. C. V. Boys, F.R.S., President, in the Chair.

A paper, entitled "*A Sensitive Magnetometer*," by Dr. P. E. Shaw and Mr. C. Hayes, was read by the former.

A torsion balance of extreme delicacy carries a pair of purest silver balls, each 3 grms. weight. A solenoid with horizontal axis passing through one of the silver balls, is brought close to the balance. On exciting the solenoid, divergent fields of known strength are obtained in the region of the ball. The resulting attraction of the ball to the solenoid is shown by a mirror reflecting a distant scale to a telescope. The couple on the torsion beam required to produce 1 mm. scale deflection is $4·5 \times 10^{-7}$ dyne cm., and this torsion balance is 10^6 times as sensitive as any known to have been used previously in this kind of work.

The results of these experiments are:—

1. The magnetic properties of the silver are ascertained even for weak fields of 1—10 gauss.

2. The silver has a pronounced retentivity; this effect being presumably due to the small trace of iron impurity.

3. The relation of susceptibility of the silver to the field used is found. The susceptibilrty of each of the constituent materials (*a*) pure silver, (*b*) residual pure iron, appears to be greatly modified by the presence of the other material.

Discussion.

Ds. S. W. J. Smith thought that the results obtained by the authors, showing the susceptibility of nearly pure silver in weak fields, were both interesting and instructive. He thought the authors, in discussing their significance, had overlooked the fact that the minute amount of iron (not exceeding 30 parts per million) shown to be present by chemical analysis, would not have the same effective susceptibility as iron in the form, for example, of long rods magnetised in the direction of their length. It was true that iron, when alloyed with other substances, could lose its characteristic ferromagnetic properties; but there was no reason to suppose that it would do so when present in silver, except in so far as the properties of a very minutely divided substance might differ from those of the same substance in bulk. So far as he knew, iron and silver were mutually insoluble. In that event the impurity found to be present should be regarded as minute particles of iron scattered about in a matrix of silver. To obtain an approximate idea of the effect of these particles upon the susceptibility of the material as a whole, it would be sufficient to regard them as spheres. Since the apparent susceptibility of a sphere is equal to $K/(1+\frac{4}{3}\pi K)$, where K is the true susceptibility, and since the true susceptibility of iron in weak fields is considerable, the apparent susceptibility of such spheres would be practically constant in weak fields and equal to $3/4\pi \div 0·24$. Hence, if the fraction of the total volume occupied by the iron were $n \times 10^{-6}$, the observed susceptibility of the material would be of the order $Ka = (0·24n - 2)10^{-6}$, where -2×10^{-6} represents the susceptibility of the silver. It was found by the authors that the susceptibility was practically constant over the range $H = 4$ to $H = 12$ c.g.s., and approximately equal to $0·25 \times 10^{-6}$. This would agree with $n \div 9·4$. In other words, the results would indicate that the amount of iron present as impurity was of the order 10 parts per million (by volume). The curves given by the authors seemed to show that the apparent susceptibility varied considerably in fields lower than $H = 4$; but part of the appearance of variability was due to the fact that, by inadvertence, the curves had been made to pass through $K_a = 0$ at $H = 0$. A possible source of uncertainty in the measurements in the weaker fields was the relatively great importance, under these circumstances, of P, the (assumed) permanent magnetism of the sphere. It seemed unlikely that the value of K for the iron in the weaker fields would be such as to make the effective susceptibility much less than $3/4\pi$, although there would be some tendency in this direction. The conclusion which he would draw from the data would be that the magnetic analysis of the material agreed with the chemical analysis and supported the inference, from other experiments, that iron and silver are mutually insoluble. The results obtained in strong fields (by Honda and others) did not, as the authors suggested, conflict with this conclusion, but confirmed it. The diamagnetic susceptibility of silver probably remains constant as the field strength is increased (within experimental limits); but, in intense fields, the susceptibility of iron is small compared with $3/4\pi$. For instance, in fields of the order 25,000 c.g.s., the value of K may be of the order 0·1 to 0·05. Taking the latter figure, the effective susceptibility of the iron spheres would be approximately 0·04. The observed susceptibility of the material as a whole would be of the order $K_a = (0{\cdot}04n - 2)10^{-6}$. Hence, assuming the value of n already deduced, we should expect K_a to be of the order $-1{\cdot}6 \times 10^{-6}$. Therefore, we should expect that the material used by the authors would become diamagnetic in strong fields. That it would, in fact, behave in such fields like the silver, of similar purity, examined by Honda.

Dr. Chree said it was of the utmost importance in working with weak fields to get rid of effects due to electric tram and railway systems. This was not an easy matter nowadays. He had expected to hear some reference to the bearing of these results on Dr. Shaw's gravitational experiments, and would like to know if the magnetic experiments had caused any modification in Dr. Shaw's conclusions on the effect of temperature on gravity.

Prof. Boys said that in his own experiments on gravitation and also in the design of the radio-micrometer, the magnetism of impurities had always to be considered. The magnetic forces involved are so minute, that in most instruments — galvanometers, for example — they are ignored. In the radio-micrometer the field that could be employed was limited by the magnetism of the purest copper that could be obtained. He had drawn some copper himself which, after being cleaned with acid and gilt to protect it from air, had worked very satisfactorily. In the case of his gravitation experiments, he had used gold balls, of the greatest purity the Mint could supply, cleaned with nitric acid. No consistent magnetic disturbances were detected on moving a permanent magnet about in their neighbourhood.

Dr. Shaw, replying for the authors, was gratified that Dr. Smith's calculations had confirmed their numerical results. His theoretical treatment had been very instructive, and had enlightened them on several important points. He would like to ask Dr. Smith if superposition of magnetic properties would still occur in the case of two mutually soluble metals?

Dr. Smith: In general, no.

Dr. Shaw, continuing, said, in reply to Dr. Chree, that in order to test whether the magnetic force between the large lead spheres and the silver spheres would vary appreciably with temperature in the gravitational experiments, he had inserted an iron bar in one of the lead spheres, but even then he had been unable to detect any variation in the force exerted on the silver when the lead and its contained rod were heated to 200° C. Since the magnetic material in the lead was very much less than this in the actual gravitation experiments, it was certain that the results were not affected by thermo-magnetic phenomena.

A paper, entitled "*The Latent Heat of Fusion of a Metal, and the Quantum-Theory*," was read by Dr. H. S. Allen.

A criticism is given of a theory of the process of fusion recently put forward by Ratnowsky. The author of the theory obtains an expression on certain assumptions for the entropy of a substance in the solid state. He then proceeds to deduce a simple formula suitable for use at high temperatures. It is shown that this formula is incorrect in consequence of the omission of a term in the expansion. Assuming, with Ratnowsky, that the entropy of the liquid state can be calculated in the same way as that of the solid, a corrected expression is deduced for the atomic heat of fusion which is equal to the difference between the entropies multiplied by the temperature of the melting-point. Ratnowsky, taking the values of the atomic heat of fusion determined experimentally, calculated the ratio of the "characteristic temperatures" for a number of metals, and came to the conclusion that the ratio is approximately constant. The values have been recalculated by the corrected formula, and it is found that they are far from constant. The ratio calculated for mercury by an independent method does not agree with the conclusion of Ratnowsky.

Some Experiments on the Thermoelectric Properties of Fused Metals were shown by Chas. R. Darling, A.R.C.S., Lecturer in Physics, Finsbury Technical College.

The experiments shown related to observations made during the progress of a research, having for its object the production of a thermoelectric pyrometer with a liquid element. If such a pyrometer could be made of suitable materials—such as graphite and molten copper—it might be possible to extend the useful range of base-metal pyrometers up to or beyond the melting-point of platinum, as the boiling-point of copper is 2310° C.

In seeking a satisfactory couple, experiments were first made with molten tin in the following manner: An iron crucible was inserted in a hole in a sheet of uralite, so that its rim was flush with the upper surface of the sheet. A groove was made in the uralite, commencing at the crucible, and the molten metal was then poured into the crucible until it overflowed, and then along the groove, at the end of which a cold junction was formed with the second metal. A wire dipping into the crucible formed the hot junction; and by this arrangement a continuous circuit was maintained between the liquid in the crucible and the solid in the groove. Advantage was taken of this arrangement to observe the effect of fusion on the E.M.F. developed, about which little information appears to exist (see paper by Porter and Simeon, *Proc.*, June, 1915). It was noted that when tin was partnered by iron, nickel, copper, constantan, or graphite, no abrupt change occurred at fusion, the E.M.F. temperature curves showing no break. Using iron and tin in this manner forms an instructive lecture experiment. Starting from the cold, the E.M.F. rises steadily; remains constant during fusion at 232°, and then rises to a maximum at 340°, after which inversion takes place—the whole change occupying only two or three minutes, when a small crucible is used.

On substituting lead, zinc, and bismuth in turn for tin, and using a variety of wires, it was again found that the change of state caused no alteration in thermoelectric properties. In the case of bismuth, however, three instances of thermoelectric "halt" were noticed, the E.M.F. attaining a maximum and then remaining unchanged over a considerable range of temperature. An iron-bismuth couple reaches a maximum of about 18 millivolts at about 250° C. (M. Pt. of Bi = 269), which remains constant to within 3 per cent up to 550°, beyond which it has not been investigated. Copper and bismuth behave in the same manner, the E.M.F. being practically the same as in the former case; whilst aluminium and bismuth furnish a third example, the E.M.F. (about 15 millivolts) being remarkably constant over a range of 300°. A previous instance of this kind was observed by Barrett with a couple of pure iron and an Fe-Ni-Mn alloy.

A suggested form of liquid-element pyrometer was described, and it was suggested that the experimental methods shown might prove useful in the thermal investigation of alloys, as the formation of definite compounds would probably be accompanied by a notable change in E.M.F. The steady E.M.F. furnished by the Bi-Al couple might also be used in work in which a constant, low E.M.F. was required.

DISCUSSION.

Dr. S. W. J. SMITH asked if there was any possibility of a chemical action occurring between the elements as the temperature increased, and so modifying the properties of the junction as to bring about the thermoelectric halt observed in some of the couples?

Prof. C. V. BOYS thought that the property must be peculiar to the bismuth, otherwise the same class of phenomenon should be obtainable with combinations of the other elements, iron, copper, and aluminium. This, of course, is not the case.

Dr. SHAW asked if Mr. Darling had used the same quantity of bismuth over and over again to see whether the results were affected by contamination?

Dr. BORNS asked if the results were repeated exactly on every occasion.

Mr. WHIPPLE thought these bismuth junctions might prove very useful sources of small constant E.M.F. for calibration purposes in works, &c.

Mr. DARLING did not think the thermoelectric halt was due to chemical action. He would like to do much more work on the subject before attempting an explanation. He had used the same bismuth many times, and the results were always the same.

A paper, entitled *Cohesion*, Part II., by Prof. H. CHATLEY, was taken as read.

OBITUARY.

SIR WILLIAM RAMSAY, F.R.S.

WE deeply regret to have to report the death of Sir William Ramsay, which occurred on July 23 at his residence at Haslemere, Bucks, after a long illness. Sir William Ramsay was one of the greatest scientific men of the day, and his death at a comparatively early age is a great loss to the civilised world.

He was born in Glasgow in 1852 and received his early education in his native place until 1870, when he went to Germany, where he studied first under Bunsen at Heidelberg and then under Fittig at Tübingen. On his return to England at the age of twenty-one he taught for a short time at Glasgow University, afterwards becoming Professor of Chemistry and finally Principal at University College, Bristol. In 1887 he was elected Professor of Chemistry at University College, London, and it was while he was there that he did the greater part of the work which has made his name illustrious. In 1913 he retired from the professorship, but at the beginning of the war he offered his services to his country in any capacity which would set free a man who could fight. He did valuable work for the empire in urging the importance of placing an embargo on cotton for Germany, upon which subject he contributed many letters to the *Times*.

Sir William Ramsay's early work dealt chiefly with organic chemistry. In 1876 he began to publish accounts of his researches on picoline and quinine and their decomposition products, but he soon turned his attention to physical and inorganic chemistry, in which his most remarkable work was done. In conjunction with Sydney Young he carried out an important series of investigations of the relationship between the vapour pressure of liquids and the temperature, and he also showed that the measurement of the surface energy of liquids enables them to be divided into two classes—those in which the molecules are simple and those which form molecular complices. In these researches he showed experimental skill in a high degree, devising some admirably neat methods and apparatus. His most famous researches, however, were those connected with the inert gases of the air. The history of the discovery of argon is well known to most chemists. In 1785 Cavendish had suggested that the air contained about 1 per cent of an unknown gas which had not then been isolated. More than a hundred years later Lord Rayleigh found that there was a constant difference in the density of atmospheric and artificial nitrogen, and thought that possibly this was to be explained by supposing that some of the diatomic molecules of nitrogen decomposed into monatomic molecules, or that atmospheric nitrogen contained some N_3 molecules. Ramsay had already discovered that nitrogen is absorbed when passed over red-hot magnesium, and he now found that if large quantities are exposed to this action a considerable increase of density of the residual gas is observed. Larger amounts were then passed through the absorption tubes, and it was finally found that a small portion remained unabsorbed. In 1894 this residue was announced by the two investigators to be a new element, an announcement which was first received with a certain amount of scepticism. The new substance was named argon from its chemical inertness, and the study of its properties occupied the attention of a number of investigators. In the following year (1895) Ramsay found that the gases which can be obtained by heating cleveite contain helium, an element which had been discovered by spectroscopy in the sun, but had hitherto not been known to exist upon the earth, although the characteristic line of its spectrum had been supposed to have been observed in a specimen of gas from a mud volcano near Vesuvius. Subsequently, Ramsay and Travers found that argon as first obtained was not an element but a mixture of elements. Two of these, krypton and xenon, were isolated by evaporating liquid air, while the third, neon, was obtained by fractionating crude liquid argon. More recently (1903) Ramsay showed that helium is one of the disintegration products of radium emanation, the α-particle expelled from radio-active matter being an atom of helium. This discovery was due to an unsuccessful attempt to examine the spectrum of the emanation. Ramsay's experiments on the transmutation of elements aroused much interest in the chemical world. By exposing salts of copper to the action of radium emanation he found that appreciable quantities of lithium were formed, while from thorium salts carbon dioxide was similarly obtained. These results, which were announced in Sir William Ramsay's Presidential Address to the Chemical Society in 1909, led to much discussion. Other investigations which occupied him at various times were the preparation of boron hydride B_3H_3, and the study of the properties of bromine, and of the decomposition products of chloroform when passed through a red-hot tube.

Sir William Ramsay's most important publications were "A System of Chemistry" (1891), "The Gases of the Atmosphere" (1896), "Modern Chemistry" (1901), and "Essays Biographical and Chemical" (1908). He was the editor of a valuable series of Text-books of Physical Chemistry.

Many honours were bestowed upon the late chemist. He was elected a Fellow of the Royal Society in 1888, and was knighted in 1902. He received a Nobel Prize for Chemistry in 1904, and was a member of many scientific societies. He was President of the British Association in 1911, and his Presidential Address, dealing with the consumption of coal and the exhaustion of the coal supply, attracted much attention. Sir William Ramsay was a man of great personal charm, and was exceedingly popular among the students who had the good fortune to work under him. He was an admirable and inspiring teacher, and many of his pupils and collaborators, among whom were Travers, Soddy, Shields, and Collie, have attained eminence in the scientific world. In the preface to the third edition of "The Gases of the Atmosphere" he wrote:—"The beginning of the twentieth century has been characterised by a revolution in chemical thought more wonderful than any which has ever been seen," and he himself did as much as any single man to bring about this revolution. His was the mind and the vigour of the pioneer, and his originality, courage, and enthusiasm made him a true leader of thought. A very great man has been taken from us at a time when we can ill afford such a loss.

THE CHEMICAL NEWS

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TWENTY-THIRD ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1915.*

By GREGORY PAUL BAXTER.

(Concluded from p. 50).

Tantalum.—Sears and Balke (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 833) have investigated the ratio $TaCl_5:5Ag$. The chloride was prepared from the oxide by distillation in a current of sulphur monochloride and the product was fractionally distilled. In Series I. the chloride was hydrolysed in a current of moist air, and the hydrochloric acid was absorbed and compared with silver. In Series II. the chloride was transferred to a stoppered platinum weighing bottle without exposure to moisture, and after being weighed it was dissolved in a large platinum flask in hydrofluoric acid solution concentrated enough to prevent the precipitation of silver tantalate. The chloride was next compared with silver. In series III. the same method of analysis was used, but the number of distillations to which the chloride was subjected varied. Vacuum weights are given in Table VII.

Table VII.

Weight $TaCl_5$.	Weight Ag.	Atomic weight Ta.
Series I.		
11·66795	17·51344	182·06
7·61398	11·42585	182·14
4·09519	6·15647	181·50
8·09039	12·16628	181·40
Series II.		
3·53605	5·31834	181·34
2·99083	4·49851	181·32
6·21118	9·34345	181·27
Series III.		
4·03892	6·07417	181·36
3·32164	5·00133	180·96
2·68304	4·04002	180·93
3·01453	4·53953	180·90
3·95846	5·95931	181·00

Table VIII.

Weight of $PbBr_2$.	Weight of Ag.	Atomic weight Pb.	Weight of AgBr.	Atomic weight Pb.
6·55858	3·85610	207·14	6·71241	207·15
4·83285	2·84126	207·17	—	—
5·67758	3·33787	207·17	—	—
6·73361	3·95874	207·16	6·89124	207·17
5·93130	3·48660	207·21	—	—
5·01729	2·94968	207·17	5·13400	207·22
5·89902	3·46730	207·25	—	—
7·71526	4·53498	207·24	7·89526	207·20
7·40244	4·35157	207·20	—	—
7·01144	4·12154	207·21	7·17470	207·21
6·91460	4·06484	207·19	7·07672	207·16
8·12623	4·77679	207·22		
Averages ..	..	207·19		207·19

The research is avowedly preliminary. The authors believe the composition of the chloride to vary with the conditions of distillation, and are at present investigating this matter.

Table IX.

Weight of $PbBr_2$.	Weight of Ag.	Atomic weight Pb.	Weight of AgBr.	Atomic weight Pb.
5·27845	3·10271	207·23	—	—
2·65094	1·55822	207·23	—	—
4·08449	2·40104	207·17	—	—
4·97508	2·92473	207·15	—	—
4·05573	2·38398	207·20	4·15017	207·18
3·44158	2·02288	207·23	3·52224	207·14
5·17416	3·04158	207·19	5·29498	207·17
3·84522	2·26022	207·21	3·93446	207·22
4·30542	2·53086	207·19	4·40616	207·15
4·53467	2·66549	207·21	4·64048	207·18
5·78467	3·40044	207·19	5·91976	207·17
4·87104	2·86337	207·19	4·98467	207·18
6·28465	3·69447	207·19	6·43124	207·19
4·74644	2·79011	207·21	4·85708	207·20
6·82444	4·01148	207·21	6·98380	207·18
6·53721	3·84274	207·20	—	—
4·10128	2·41088	207·18	4·19791	(207·09)
2·64271	1·55352	207·18	—	—
6·30717	3·70718	207·23	—	—
Averages ..	..	207·20		207·18

Table X.—Cl = 35·457.

Weight of $PbCl_2$.	Weight of Ag.	Atomic weight Pb.	Weight of AgCl.	Atomic weight Pb.
Commercial nitrate—				
5·63567	4·37200	207·21	—	—
5·58730	4·33427	207·22	—	—
6·86319	5·32402	207·22	—	—
Galena (Joplin, Mo., U.S.A.)—				
4·70770	3·65223	207·20	—	—
4·20222	3·25968	207·23	—	—
Cerussite (Wallace, Id., U.S.A.)—				
7·04688	5·46691	207·20	—	—
5·88935	4·56868	207·22	—	—
6·96370	—	—	7·17754	207·22
6·89046	—	—	7·10231	207·21
Vanadinite and wulfenite (Tucson, Ariz., U.S.A.)—				
4·90083	3·80171	207·22	—	—
5·79300	4·49404	207·21	—	—
Galena (Metalline Falls, Wash., U.S.A.)—				
5·43965	4·21992	207·21	—	—
5·74504	4·45674	207·22	—	—
Galena (Nassau, Germany)—				
6·57216	5·09849	207·21	—	—
5·66330	4·39340	207·21	—	—
Cerussite (Eifel Mts., Germany)—				
5·73434	4·44857	207·21	—	—
4·17445	3·23862	207·19	—	—
Cerussite (New South Wales)—				
6·25884	4·85584	207·19	—	
5·25882	4·07933	207·23	—	—
7·33227	—	—	7·55732	207·22
6·51699	—	—	6·71690	207·23
Averages ..	..	207·21		207·22

Lead.—Non-radio-active lead has been investigated by Baxter and Thorvaldson (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1020) and Baxter and Grover (*Proc. Nat. Acad.*, 1915, i., 71; *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1027). The first-named compared lead bromide, which had been fused in an atmosphere containing hydrobromic acid, with silver and silver bromide. Br = 79·916. Weights are corrected to vacuum (Table VIII.).

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* *Journal of the American Chemical Society*, xxxviii., No. 3.

In a similar series of experiments Baxter and Grover corrected for a trace of insoluble material in the fused lead bromide, which is neglected in the above series. The outcome of the two series is essentially the same (Table IX.).

In order to determine whether common lead always possesses the same atomic weight Baxter and Grover also analysed lead chloride which had been prepared from minerals from known widely different geographical sources. None of the material was radio-active (Table X.).

The average of all the different series of results is 207·20. This value is perceptibly higher than that obtained some years ago by Baxter and Wilson.

Radio-active Lead.—Hönigschmid and Mdme. St. Horovitz (*Sitzb. k. Akad. Wien.*, Abt. II., A, 1914, cxxiii., 1; *Monatsh.*, 1915, xxxvi., 355) have continued their investigation upon radio-active lead by analysis of lead chloride prepared from carefully selected minerals (Table XI.)

TABLE XI.

Weight of $PbCl_2$.	Weight of Ag.	Atomic weight Pb.	Weight of AgCl.	Atomic weight Pb.
St. Joachimsthal Pitchblende—				
2·91224	—	—	3·01042	206·410
2·47886	—	—	2·56256	206·396
2·76797	—	—	2·86126	206·413
		Average		206·405
Crystallised uranium oxide (Morogoro, German E. Africa)—				
3·24177	2·52563	206·024	3·35537	206·054
3·94867	3·07636	206·025	4·08686	206·066
3·78263	2·94693	206·033	3·91519	206·053
3·68899	2·87400	206·030	3·81830	206·052
4·49731	3·50343	206·054	4·65464	206·070
Averages.. ..		206·033		206·059
Bröggerite (Moos, Norway)—				
4·50069	—	—	4·65794	206·082
4·49363	—	—	4·65060	206·084
Average				206·083
Bröggerite (Moos, Norway), distilled $PbCl_2$—				
4·83605	3·76724	206·060	5·00512	206·076
3·97826	3·09903	206 060	4·11741	206·072
4·91204	3·82647	206·057	5·08425	206·050
Averages.. ..		206·059		206·066
Common lead, distilled $PbCl_2$ —				
6·17861	4·79374	207·177	6·36895	207·193
4·75170	3·68659	207·182	4·89837	207·176
4·83397	3·75047	207·178	4·98328	207·170
Averages.. ..		207·179		207·180

The leads from Morogoro and Moos possess a lower atomic weight than any other specimen of radio-active lead which has been examined.

Guye and Germann (*Comptes Rendus*, 1914, clix., 992) have calculated the effect on various atomic weights of the gaseous impurities which they have found in silver (see Twenty-second Annual Report; also *Comptes Rendus*, 1914, clix., 225). Inasmuch as their investigations were not carried out with silver prepared with the care necessary for atomic weight experiments, it is premature to rely upon the corrections which they compute.

The idiosyncrasies of the silver coulometer have been further investigated by Richards and Anderegg (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 675), and Hulett and Vinal *Journ. Phys. Chem.*, 1915, xix., 173).

BARIUM IN TOBACCO AND OTHER PLANTS.

By BONNIBEL ARTIS and HAROLD L. MAXWELL.

SCHULE, in 1788, first observed the presence of barium in plants, obtaining it from beech trees. Forchammer, in 1855, detected it in the ashes of beech, oak, and birch trees. In the same year, Eckhard and Boëdeker confirmed its existence in beech wood, and also found it in the sandstone near Goettingen.

In 1874, Knop, of Leipzig, while investigating the mud carried down by the River Nile, found that barium was present. The following year Dwarzak confirmed the presence of barium in the Nile mud, and also found it in the leaves, ear, and stalk of wheat grown in the Nile valley.

A number of investigations have been made in the United States for the detection of barium by the Bureau of Plant Industry and the Bureau of Soils. The work in this country has been done to ascertain, if possible, if the poisonous properties of the loco weed, which causes the loco disease in cattle, is due to the presence of barium in plants.

J. S. McHargue (*Journ. Am. Chem. Soc.*, June, 1913) describes his work that shows the presence of barium in tobacco and in various other plants.

Many are doubtless more or less familiar with the wide distribution of barium in soils. The simpler compounds into which the old igneous rocks have disintegrated finally became available for plant food, and have been assimilated by the growing plant. It is still a question whether barium should be considered a plant food at all, although it is found more or less in the vegetable kingdom, but not in all the species that have been investigated.

We have examined the leaves and stems of a number of specimens of tobacco grown in Cuba and Sumatra and in various parts of the United States. We desire to express our thanks to Mr. J. M. Goldstein, of Oneida, New York, for kindly supplying most of the specimens.

Our method was essentially that outlined by McHargue in the paper referred to. We selected 25 grms. of the leaves which were just sufficiently moist to prevent crumbling. These were cut into small bits, and placed under a hood, as the odours are very disagreeable. The combustion is made with one Tirrell burner in about two hours. Too great heat is not desirable as it fuses the ash and renders it more difficult to handle. The ash is weighed, and while in the platinum dish it is damped with distilled water, 15 cc. of dilute hydrochloric acid is added, and it is left on the water-bath twenty minutes to complete the reaction. There are two conditions in which the barium seems to exist in the ash—a part soluble in hydrochloric acid and an insoluble portion which is barium sulphate. The precipitate containing the barium sulphate with the ashes of the filter-paper is placed in a platinum crucible, to which are added a few drops of dilute sulphuric acid and 10 cc. of hydrofluoric acid. It is digested slowly for several hours over a free flame. This decomposes the silicates, and the residue is evaporated to dryness. Next an alkali fusion is made with about 4 grms. of pure sodium carbonate to decompose the barium sulphate. The residue is changed to barium chloride with hydrochloric acid, and added to the first hydrochloric acid fitrate. The solution is heated to boiling, and the barium is precipitated in the usual way with a few drops of dilute sulphuric acid. We treated the stems in the same way. The ash is chiefly carbonates, and we experienced difficulty in securing a constant weight, as the CO_2 would be driven off by the heat. The per cent of the ash represents the mean of two or more determinations. (Table I.).

These leaves were gathered in autumn at the time of their full maturity. The results are given in Table II.).

The determinations given in Table III. were made from immature leaves, gathered in May soon after their appearance.

The leaves were gathered from trees or shrubs on the Cornell College Campus, or from the village of Mount

Vernon. An analysis of soil from the Campus gave 0·1312 per cent of barium sulphate.

TABLE I.

Kind of tobacco.	Ash. Per cent.	$BaSO_4$ in the plant. Per cent.
Havana tobacco from Cuba—		
Leaf	20·85	0·0608
Stem	25·68	0·0760
Broad leaf grown in Pennsylvania—		
Leaf	21·98	0·0648
Stem	21·62	0·0780
Havana seed grown in Connecticut (under canvas tents)—		
Leaf	20·11	0·0600
Stem	19·38	0·0720
Pennsylvania tobacco, grown in Pennsylvania—		
Leaf	21·48	0·0980
Stem	24·28	0·1280
Sumatra tobacco—		
Leaf	20·87	0·0308
Stem	24·73	0·0408
Wisconsin tobacco, grown in Wisconsin—		
Leaf	21·62	0·0192
Stem	24·49	0·0280
Tobacco from farm of Leon Bequillard, Mexico, New York—		
Leaf	—	0·0132
Stem	—	0·504

TABLE II.

Kind of leaf.	$BaSO_4$ (per cent).
Dogwood	0·0224
Cotton wood	0·0052
Cherry	0·0392
Black locust	0·0324
Mulberry	0·0696
Elm	0·0356
Linden	0·0152
Wild olive	0·0048
Plum	0·0372
Box elder	0·0360
Hard maple	0·0368
Walnut	0·0752
Pear	0·0196

TABLE III.

Kind.	Grms. taken.	$BaSO_4$ (per cent).
Soft maple	6·2190	0·0273
Wild grape	6·3755	0·0941
Wild cherry	2·9758	0·0336
Box elder	3·3790	0·0295
Cotton wood	3·7857	0·0528
Lime	5·9628	0·0435
Cherry	8·9432	0·0134
Elderberry	9·0887	0·0143
Black walnut	12·3913	0·0096
Sumac	9·9845	0·0071
Elm	10·4115	0·0182
Blackberry	8·1130	0·0086

We desire to express our thanks to Dr. N. Knight for suggestions and help in this work.

Cornell College, July 4, 1916.

Arts and Crafts Exhibition.—An exhibition of the Arts and Crafts Exhibition Society will be held next October in the Galleries of the Royal Academy. The address of the Secretary, Prof. E. S. Prior, is 1, Hare Court, Temple, E.C.

THE DETERMINATION OF METHYL AND ETHYL ALCOHOL IN SPIRIT VARNISHES.*

By G. W. KNIGHT and C. T. LINCOLN.

(Concluded from p. 58).

SIMILAR mixtures of the iodides obtained from mixtures of the alcohols containing 11 per cent of methyl alcohol were distilled on the same day under similar atmospheric conditions, and in the same manner as above with concordant results. The first drop was collected at 60·3° C. in each case, and the distillate collected below 69° C. measured 5·0 cc. in one case and 5·1 cc. in the other.

Other mixtures made from alcohol containing 10 per cent of methyl alcohol, but distilled on different days under different atmospheric conditions, gave, in one case, first drop at 60·0° C. and distillate below 69° C., 4·7 cc.; in the other case, first drop at 62·2° C. and distillate below 69° C., 4·3 cc. The method was further tested with other mixtures, hut the results were concordant only within varying limits, owing to conditions over which we had no control, and to correct for which would entail a considerable amount of tedious calculations. The method appears to have the same faults as the ebullioscope method for the determination of ethyl alcohol, with added difficulties (Leach, "Food Inspection and Analysis," 1904, p. 545).

In the hope of developing a method that would be simpler and at the same time eliminate variations due to different atmospheric conditions and different types of apparatus, as well as obviate the necessity of working out empirical figures for each percentage content of alcohol, the writers investigated the specific gravity of the iodides and mixtures of the same. The literature was consulted with the following results:—

Wirthle gives the sp. gr. of methyl iodide as 2·295 (15°/15° C.) and ethyl iodide 1·943 (15°/15° C.), but he did not attempt to determine the percentages of the constituents by difference in density.

Other investigators determined the specific gravities as follows:—For methyl iodide, Perkins found at 15° C., 2·28517, at 25° 2·25288 (*Journ. Pr.*, [2], xxxi., 500); Pierre at (15°/15° C.), 2·28517 (*Ann.*, lvi., 147), Bardy and Bordet at (15°/15° C.), 2·2677 (*Ann. Chim. Phys.*, [V.), xvi., 569); for ethyl iodide, Perkins found at 15° C. 1·94332, at 25° C. 1·92431; Mendeléeff at 15° C., 1·9309; Linnemann at 14·5° C., 1·9444, corrected to 15° C., 1·9434.

These figures show that both iodides have a relatively high coefficient of expansion, and this fact, together with the volatility of the liquids, undoubtedly explains the lack of uniformity in the results of different investigators. A difference of 10° C. between 15° C. and 25° C. makes a difference in sp. gr. of about 0·02 in the case of ethyl iodide, and about 0·03 in the case of methyl iodide, while with water between the same limits a difference of only 0·002.

The writers obtained the following results:—

Methyl iodide, specific gravity	(15·6°/15·6° C.)	2·2920
	(25°/25° C.)	2·2700
Ethyl iodide, specific gravity	(15·6°/15·6° C.)	1·9470
	(25°/25° C.)	1·9300

These results agree fairly well with those reported by Wirthle.

A number of mixtures of the alcohols containing varying percentages of methyl and ethyl alcohol, some without acetone and some containing up to 20 per cent of crude acetone, were analysed, and formulæ were worked out and simplified for the calculation of the percentages by volume of methyl and ethyl alcohol from the specific gravity of the iodides. In no case was there a great variation from the amount of the alcohols known to be present.

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* Contributed with the permission of the Secretary of the Treasury and the U.S Appraiser, Port of New York. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 10

The Riche and Bardy method was carefully studied, and the conditions and modifications necessary for making it available for a quantitative determination of methyl alcohol for quantities up to 10 per cent worked out.

Spirit varnishes were made up containing Columbian spirits, crude wood alcohol, grain alcohol, oil of turpentine, pyridine, ammonia water, aniline dyes, crude acetone, and varnish resin. Varying proportions of the different constituents were put into each varnish. They were then analysed by the method given below with satisfactory results, none of the above mentioned constituents, all of which may occur in commercial spirit varnishes, interfering with the accuracy of the process to a noticeable extent.

Method.

(In the absence of acetone and pyridine use the modification of the Leach and Lythgoe method described above).

Distil a quantity of the varnish, accurately measured at 15·6° C., sufficient to give at least 25 cc. of distillate. Place the varnish in a distilling flask, having the bulb immersed in a steam-bath, the side tube connected with a Liebig condenser, and the top connected with an aspirator bottle by a tube which has a glass cock attached, and passes through a rubber stopper into the bulb of the flask. Collect the distillate in an accurately graduated measuring cylinder, immersed in ice-water, and connected with the condenser by an adapter, and with a Péligot tube containing water by a piece of bent glass tubing.

When the distillate ceases to come over pass air through the apparatus from the aspirator bottle until no more liquid distils. Allow the distillate to assume a temperature of 15·6° C., and read the volume accurately. (If the distillate contains amyl or higher alcohols or esters, detected by the odour, they must be removed by the Thorpe and Holmes method, and re-distilled over anhydrous potassium carbonate until the final distillate contains less than 50 per cent of water).

Test the distillate for methyl alcohol as follows:—

Dilute 1 cc. of the distillate to 10 cc. with water, and then to 5 cc. of this solution, contained in a wide test-tube, add 2½ cc. of a 2 per cent solution of potassium permanganate, and then 0·2 cc. of concentrated sulphuric acid. After three minutes add 0·5 cc. of saturated oxalic acid solution and shake. Then add 1 cc. of concentrated sulphuric acid, and immediately afterwards 5 cc. of Schiff's reagent (Mulliken's "Identification of Organic Compounds," i., 15). If methyl alcohol is present in the varnish a violet coloration appears in a few minutes. All reagents should be accurately measured in a pipette graduated to hundredths of a cc.

Test another portion of the distillate for ethyl alcohol in the following manner:—

Heat 0·2 cc. of the distillate and 5 cc. of bromine water (0·3 cc. bromine in 50 cc. of water) in a boiling water-bath for five or six minutes. Cool the mixture, and, if still coloured, add 10 per cent sodium bisulphite solution drop by drop until the colour just disappears, and then 5 cc. of Schiff's reagent. A red or reddish violet coloration indicates the presence of ethyl alcohol.

Place 20 cc. of water, and 80 grms. of powdered iodine in a 125 cc. distilling flask (in case the first distillate had to be purified to remove amyl compounds or the distillate contains an appreciable amount of water, use in place of 20 cc. of water such an amount that the final mixture in the flask contains not more than 50 per cent of water). Immerse the flask in ice-water. Add 20 cc. of the distillate measured at 15·6° C., connect the side-tube of the flask with a long condenser, and the upper end of the condenser with a Péligot tube containing some water. Stopper the flask, and allow the mixture to stand fifteen minutes with occasional gentle shaking of contents. Then add 8 grms. of red phosphorus, stopper the flask, and tip the condenser till it is inclined upward and forms a reflux condenser connected with the flask by the side-tube. Keep the temperature of the mixture in the flask sufficiently low by immersion of the flask in ice-water to prevent loss by volatilisation. When the reaction has ceased replace the ice-water bath by a water-bath, and gradually heat the water to 75° C., being careful not to heat the flask so rapidly that any of the volatile constituents pass into the Péligot tube. Heat at 75° C. for about twenty minutes. Then allow the contents of the flask to cool to room temperature. Tip the condenser so that it inclines downward instead of upward, and connect the lower end with an adapter through a rubber stopper with a carefully calibrated measuring cylinder which is immersed in ice-water, and connected with a safety valve in the form of a Péligot tube containing water. Place 30 cc. of water in the measuring cylinder, replace the stopper in the flask with a cork carrying a glass tube fitted with a glass cock (closed), and connected with an aspirator bottle. Heat the flask gently at first, then with increasing heat until most of the volatile matter has passed over, collecting the distillate under the water in the cylinder. Then raise the adapter till it dips into the water layer but does not enter the iodide layer, open the stopcock, and pass air through the apparatus until no more distils over. Allow the distillate to assume a temperature of 15·6° C., and read the volume carefully.

I.—If the preliminary tests of the first alcoholic distillate show the absence of methyl alcohol, the percentage of ethyl alcohol in the varnish may now be calculated by the formula:—

$$\text{Per cent ethyl alcohol in varnish} = \frac{3{\cdot}622\, V_1 V_3}{V}.$$

Where V = volume of varnish used
V_1 = volume of alcoholic distillate
and—
V_3 = volume of iodides obtained.

II.—If the alcoholic distillate contains no ethyl alcohol,—

$$\text{Per cent methyl alcohol in varnish} = \frac{3{\cdot}315\, V_1 V_3}{V}.$$

III.—When both ethyl and methyl alcohol are present together,—

$$\text{Per cent total alcohol} = \frac{(0{\cdot}03315\alpha + 0{\cdot}03622\beta)\, V_1 V_3}{V}.$$

Where α = per cent of methyl alcohol by volume of total alcohol, and
β = per cent of ethyl alcohol by volume of total alcohol.

The values α and β are determined by the following procedure:—Transfer the contents of the measuring cylinder into a separatory funnel, add 3 cc. of 10 per cent $NaOH$ solution, and shake. Separate the iodides from the aqueous layer, and wash in another separatory funnel with small quantities of ice cold 1 per cent $NaOH$ solution until the iodides are absolutely colourless. Draw off the washed iodides into a 50 cc. Erlenmeyer flask, add a few grms. of recently heated potassium carbonate, stopper the flask, and let it stand, immersed in ice-water, with occasional shaking, for about half-an-hour. Filter into another 50 cc. Erlenmeyer flask, taking precautions to prevent evaporation by using a funnel that fits the neck of the flask perfectly, and covering the funnel with a watch-glass. Stopper the flask, immerse in ice-water, and use the purified product thus obtained for the accurate determination of the specific gravity of the mixed iodides at 15·6° C. (Where time permits it would be well to run blanks for specific gravity determinations, with absolute methyl and ethyl alcohols, to prevent differences that usually occur with different operators owing to personal equation, &c.).

IV.—From the specific gravity thus obtained calculate the percentage by volume of methyl alcohol in total alcohol (a) by the following formula:—

$$\text{Per cent methyl alcohol} = \frac{3905\,(G - G_2)}{39{\cdot}05\,(G - G_2) + 51{\cdot}25\,(G_1 - G)}.$$

Where G = specific gravity (15·6°/15·6° C.) of mixed iodides,

G_1 = 2·292; specific gravity (15·6°/15·6° C.) of methyl iodide, and

G_2 = 1·947; specific gravity (15·6°/15·6° C.) of ethyl iodide.

Subtracting the percentage of methyl alcohol thus obtained from 100 gives the percentage of ethyl alcohol (b). From these values the percentage of total alcohol by volume is readily calculated by Formula III., and then the percentage by volume of each in the varnish.

If the percentage of methyl alcohol in total alcohol falls below 10 per cent, the following procedure based on the Riche and Bardy method for the detection of methyl alcohol will be found to give quantitative results of greater accuracy than is possible by the specific gravity method.

Two standard solutions, one of absolute ethyl alcohol and the other containing a mixture of 10 per cent by volume of absolute methyl alcohol and 90 per cent by volume of absolute ethyl alcohol, are treated to form the iodides, and distilled and purified as described above, and then subjected to the following treatment together with the unknown:—

Place 5 cc. of the iodides with an equal volume of aniline in a 200 cc. narrow neck flask, stopper the flask, and allow to stand over night in a dish of water at room temperature. In the morning add 150 cc. of water, heat till the water just begins to boil, add about 30 cc. of 10 per cent caustic soda solution, and then water until the light oily layer of dimethyl and diethyl aniline is brought into the neck of the flask. Pipette 1 cc. of the oily layer into a small porcelain dish, and mix it well with 10 grms. of an intimate mixture of 100 parts of clean sand, 3 parts of finely powdered cupric nitrate (see Note), and 2 parts of finely powdered sodium chloride. Heat the dish in an oven at 90° C. for about eight hours, occasionally stirring the mixture, and breaking up the lumps that may form. Then transfer the entire contents of the dish to a 100 cc. graduated flask with hot 95 per cent alcohol, using not more than 80 cc. of alcohol in all, and boil for about twenty minutes. Cool the flask, make up to the mark with 95 per cent alcohol, shake, allow to settle, pipette 1 cc. of the solution into a 500 cc. graduated flask, and fill up to the mark with water.

(Note.—The cupric nitrate must be very finely powdered, and the component parts must be intimately mixed in order to make the colorimetric test sufficiently delicate for quantitative work, and the mixture used for the standards must be identical with that used for the unknown determination, since different mixtures give different intensities of colour with the same quantity of dimethyl aniline).

By mixing the standard solutions thus obtained from the absolute ethyl alcohol and the mixture containing 90 per cent of ethyl alcohol and 10 per cent of methyl alcohol in the proper proportions, make up standards ranging from 1 per cent methyl alcohol to 9 per cent methyl alcohol, leaving enough of the initial standards to use for comparison also. Now compare the unknown solution with these standards either in Nessler tubes or a suitable colorimeter. In case the unknown has a tint between any two of the standards, by further dilution of these the percentage can be determined to tenths of a per cent. If the shade of the unknown is deeper than the 10 per cent standard, it may be matched with the standard by dilution, but the variation from the standard must not be great or the method becomes inaccurate.

CHEMISTRY AND ENGINEERING, CO-OPERATION BETWEEN.

An article by Prof. F. G. Donnan, F.R.S., upon the necessity for co-operation between the engineer and the chemist, which appears in the *Times Engineering Supplement* for July 28, 1916, contains so much practical common sense that we cannot refrain from quoting from it and reproducing the latter portion, so as to bring it before those of our readers who may not happen to have read the original. First drawing attention to an anomaly of which chemists are painfully aware, namely, that although in the study of engineering as conducted in our universities and technical schools, the study of applied physics is recognised as essential, corresponding departments of applied chemistry are practically non-existent.

The importance of physical chemistry in the "coming crash of peace" cannot well be over-estimated. The design, control, and running of chemical plant and processes on a factory scale consists in three things—physical chemistry, applied physical chemistry, and ordinary mechanical engineering. There undoubtedly is great need of men properly trained for such work. It is often argued that in the training and practice of chemistry there is no time for "engineering." Such a view is wholly mistaken. It is suggested that in the present state of things the young chemist is often overburdened by "useless memorising and molecule-juggling."

Having discussed the need for laboratories of applied chemistry and drawn attention to many changes that will be necessary in the training of chemists if Great Britain is to hold her own in the chemical industry of the future, Prof. Donnan discusses the second part of the misunderstanding, which consists in the failure to realise that the laboratory of applied chemistry here advocated is not intended to be a place where the descriptive particulars of any special or particular type of chemical industry are exclusively taught. Some laboratories of this type do exist in the country and are of value in producing a better class of skilled foremen for special trades, but we cannot and must not regard them as in any sense comparable with the great departments of engineering. When we speak here of a laboratory or department of applied chemistry we mean a place where the general scientific principles underlying the design, construction, testing, and control of chemical plant and processes shall be taught in a manner comparable in thoroughness and scientific quality with the fine methods and traditions of the great British schools of engineering. There exists here not only an urgent necessity but a magnificent opportunity. We do not possess the great higher technical schools of Germany, but, contrary to the practice of that country, we have schools of engineering attached to all our great universities. Hitherto our chemists and engineers have been kept apart, with extraordinary disadvantage to both sides, whereas in the great German higher technical schools the necessary link has long been forged. From this combination has issued the host of men in Germany who apply chemical science to practice. They are not as a rule the pioneer discoverers of new chemical substances—that is the business of the skilled molecule-juggler in his laboratory—but they are the men through whose patient and untiring work the ideas and results of the pioneer discoverers are converted into the fine gold of successful practice.

Here lies one of the secrets of German success in chemical industry, a secret not usually recognised, though of the very highest importance. There are other factors it is true, such as expert scientific leaders of industry, an abundance of skilled industrious workmen who are not pledged by a vicious form of trade unionism to limit their output, and an alert and far-seeing Government conscious of the value of scientific knowledge and quick to foster and encourage industrial enterprise by every feasible method. But the factor with which we are dealing here is of great and constantly growing importance. The old style of chemical engineering is as dead as a door-mat. The modern appliers of chemical science must be thoroughly and scientifically trained and able to "think big" in order to cope with the rapidly growing size, complexity, and refinement of chemical engineering—that is, applied chemistry.

The Dead Hand of Examinations.—What we require to do, therefore, is to bridge the gap which exists between our present chemical and engineering laboratories by "inter-linking" laboratories of chemical engineering. Here will meet and work together the young chemists and the young engineers who intend to enter the field of applied chemistry. If they have each received the preliminary grounding dealt with earlier they will be ready to combine in this field, to their immense common advantage. A vista of magnificent possibilities lies before us here. What, then, can possibly hinder such an urgently necessary and easily accomplished development?

The answer is, alas! only too obvious—the cold, dead hand of the British examination degree system, which in a perpetual and dread *rigor mortis* grips the living flesh of our youth. And the curious fact is that the more modern and newly founded a British university is the more it suspects its professors and the more it seeks to save its soul by the scheduled manufacture of "examination degrees" rather than the unfettered training of men and the free pursuit of knowledge. This is the monstrous thing which stretches out its dead fingers and separates the university laboratory from the living world of manufacture and industry. Its deadening influence devitalises and depresses the whole country. Grant a mark of rank for honest productive work, and let the professor be the sole judge thereof. Judge him by the work and careers of his pupils and not by the musty records of the university's "degree lists." If you cannot trust him why appoint him? Let us get rid of all the immense and useless machinery of British university examinations, whose infinite cogs and wheels perpetually grind and produce nothing. Let us get into touch with life and reality, let in the breath of freedom, and cast out this dead relic of illusion and delusion.

At the present moment the pulse of awakening life and progress is beginning to throb in the country. Chemical manufacturers and manufacturing engineers are beginning to form themselves into groups and associations. It is beginning to be realised that it is better for Jones and Smith to combine against clever and well-organised Schmidt and Company than to spend their time exclusively in fighting each other. There is also considerable hope that when Jones and Smith, representing some hundreds if not thousands of millions of capital, have had a heart-to-heart talk with those distinguished gentlemen whose destiny it is to guide the policy and fortunes of the British Empire, the results of the conversation will be of benefit to the said empire. But no amount of business acumen, of judicious industrial combination, or of alert and far-seeing Government policy will be of the slightest avail unless the land is flowing with the milk and honey of scientific production. The makers and the appliers of scientific knowledge must be given the maximum of encouragement, freedom, and recompense. Jones and Smith must know and value them, and they must know and value Jones and Smith. Nought must stand between the twain, whose union in mutual respect and esteem will assuredly constitute one of the impregnable bulwarks of the British Empire.

Application of Scientific Principles.—Space does not permit any elaborate discussion of the nature of the work and the best mode of carrying it out which would be appropriate to the laboratories of applied chemistry, but the ruling idea must be the application of scientific principles to the design and control of plant and processes. It will be of no avail to buy pieces of chemical plant and machinery, fire up the furnaces, and trust to Providence and expensive experience to do the rest. The would-be applier of chemistry must be taught, as the young engineer is at present taught, to go back to the simple principles of science, and to apply these at every point to the problems of design, construction, and control. He must be accustomed to figure out at every stage the efficiency as regards both energy and materials. For every process and every piece of plant he studies he must work out complete balance-sheets for energy and for material. There must be no vague and uncertain losses, the amounts of which he does not know and the causes of which are not thoroughly clear to him. In a word, it must be good engineering science and not chemical rule-of-thumb.

Theory and Practice.—A moment's consideration of these matters will suffice to dispel one of the most persistent and curious fallacies. It is often arged that the university chemist is too "theoretical" and does not understand "practical" matters. Let us analyse this argument, for it is of great importance. The university chemist does understand "practice," but it is the practice of molecule-juggling—that is to say, the practice of the analysis and synthesis of chemical substances in the laboratory. In this extremely important business he is not only a skilled theorist but a skilled practician. What he does not usually understand is another theory and another practice—namely, the theory and the practice of designing chemical engineering plant and conducting and controlling chemical processes in a factory. What is wanted in the country is the production of many young men who have received a thorough preparatory training in this second and equally important theory and practice. There is never any conflict between "theory" and "practice." The failure to realise this is one of our besetting intellectual sins, and is based on an entire confusion of thought. This mental fog has been more or less dispersed in the profession of engineering; it is high time that it were dispersed in the profession of applied chemistry.

SULPHATE OF AMMONIA ASSOCIATION.

Second Annual Report.

The Executive Committee beg to submit to Subscribers the Second Annual Report of the Sulphate of Ammonia Association with which is incorporated the Nineteenth Annual Report of the Propaganda Committee, together with a Statement of Accounts for the financial year ended June 30, 1916.

We are pleased to be able to state that the Association has extended the scope of its work in every direction, and has now come to be generally regarded as the representative and defender of manufacturers' interests in all matters germane to the production of sulphate of ammonia.

The Minister of Munitions has constantly sought our assistance and advice upon general and technical questions, and we have naturally made every endeavour to meet its wishes in every way.

With the Boards of Trade and Agriculture we have at times unfortunately found ourselves in disagreement. While we were unable to prevent these Departments from enforcing a total prohibition of export during the spring months, thereby causing irreparable loss to the country and great inconvenience to manufacturers, the event has so far proved the soundness and correctness of the suggestions and estimates we offered them regarding the method of issuing licences and the quantities required by home agriculture as to predispose them favourably towards making more businesslike arrangements for the coming season.

Our efforts to secure a limitation of prices for sulphuric acid met with better success, and we think we may fairly claim that it was our action which led the Ministry of Munitions to fix the maximum prices now in force.

The activities of the selling branch have been considerably extended, the number of manufacturers who have entrusted us with the entire sale of their sulphate of ammonia has increased, and the quantity sold for other members has also increased, so that the tonnage disposed of during the year is very considerably greater than the total sales last year. Apart from this a large number of manufacturers who prefer still to retain sales in their own hands make a practice of consulting us before selling. The volume of business transacted directly with consumers has also increased, among the contracts secured being one with the French Government for the supply of sulphate of ammonia for munitions.

Weekly reports and lists of sales have been issued to members of the selling branch, and in addition to this we have from time to time circulated valuable information concerning matters affecting the trade with special reference to the increase in production of nitrogen in Germany.

We think we may claim therefore that the selling branch has continued to fulfil a useful function, and in support of this view we may point to the increase in the tonnage contributing to this branch from new members, amounting to 8228 tons. The total tonnage contributing to this branch now exceeds last year's by over 10,000 tons.

In our last report we drew special attention to the question of quality. Allowing for the difficulties experienced in obtaining the right qualities of sulphuric acid, we think that the effect of our pamphlets and suggestions is beginning to be felt, and that the quality of sulphate produced has improved on an average. There is still room for further improvement, however, and we trust that all our members will make due preparation now so that as soon as conditions are again normal they will be able to produce 25 per cent sulphate of ammonia in good mechanical condition. We also wish to draw special attention to the desirability of employing strong bags of good outward appearance for home sales.

Members have shown a growing disposition to seek the assistance of our expert in the manufacture of sulphate of ammonia, and Mr. Clark has devoted as much time to our work as his duties with the Royal Naval Air Service allowed.

The work of the selling branch has been intimately associated with that of the propaganda branch, and, as foreshadowed in last year's report, greater attention has been devoted to commercial questions.

In accordance with the decision of the Propaganda Committee, certain alterations are being carried out in the organisation of the outdoor staff with the idea of increasing the efficiency of the Association as a distributing agency without interfering with its scientific activities.

Our efforts to interest corn and manure merchants in sulphate of ammonia have met with marked success, and the steps which have been taken to maintain uniform prices over large districts for a month and more at a time have undoubtedly greatly assisted sales. The fact that the prices charged to farmers and manure merchants have been on an average about 30s. per ton below the export selling value is sufficient reply to our numerous critics in Parliament and elsewhere who have accused the Association of constituting a ring whose sole object is the forcing up of prices.

From the figures and estimates obtained we are able to report that the increase in the quantity of sulphate of ammonia used by home agriculture last season was over 10 per cent in excess of the tonnage taken in previous years. Although this increase is not as large as we could have wished, we think that the result is satisfactory when the innate conservatism of farmers, the exceptionally bad weather, the reduction in the acreage of green crops, and the scarcity of labour are taken into account. Although the actual increased quantity used is not very large, we are convinced that a larger number of individuals than ever before have used sulphate of ammonia, and we confidently expect that this will form the basis for a large development in the future.

We may mention in particular that the autumn application of sulphate of ammonia to wheat has proved a great success in a large number of cases, thus proving that, generally speaking, our soils are more retentive than has hitherto been admitted by science. In recommending this the Association undertook a somewhat venturesome step, and we wish to record our sense of obligation to the Board of Agriculture for lending us its support for the introduction of this novel practice.

Field Experiments.—In conformity with the alteration of policy decided by the committee, fewer manurial experiments have been carried out this season, the expenditure under this heading amounting to about half the sum spent last year. In future we intend to make fewer experiments but on larger areas, and with a few of solving particular problems, as we feel certain that our experimental work in past years has amply demonstrated the general value of sulphate of ammonia throughout the country. Farmers, indeed, generally appreciate its value, but confine its use to specific crops and times of application.

Literature.—A large quantity of literature of all descriptions was distributed throughout the season. 2000 copies of our Brochure, "The Market for Sulphate of Ammonia and its Future," dealing with the achievements and aims of the Association were circulated, and the demand for our complementary pamphlets, "Does it pay to make 25 per cent Ammonia?" and "Suggestions for the Manufacture of High Testing Sulphate of Ammonia," created such interest that 4000 copies of each were distributed. All these issues met with a very cordial reception at the hands of subscribers and other manufacturers. The propaganda branch issued pamphlets entitled "The Manure Richest in Nitrogen," of which 125,000 copies were circulated, and "Luxurious Growth," a highly illustrated pamphlet, of which 20,000 copies were sent out. In addition to this, 400,000 copies of a leaflet, "To Farmers," were circulated mainly through corn and manure merchants early in January. A large number of the Board of Agriculture's leaflets advocating the use of sulphate of ammonia was also distributed. With a view to facilitating the purchase of supplies by corn and manure merchants, classified lists of producers throughout the country were prepared, and there was a large demand for these. The demand for the pamphlet, "Artificial Manures for the Farm, Small Holding, and Garden," continues, and several thousand copies have been distributed during the season. As the circulation of this pamphlet was causing some offence to manure mixers a slip has been attached advising buyers to apply to mixers for the manures advocated.

Advertising.—In view of the restriction in the number of experiments it was thought well to continue to advertise on a very extensive scale and the expenditure under this heading has been slightly heavier than last year. Advertisements, articles, and insertions have appeared in 22 different agricultural journals, and a beautifully illustrated supplement dealing with the production and use of sulphate of ammonia was published by arrangement with *Country Life.* We feel sure we shall reap the benefit of these efforts very soon.

In view of the shortage of supplies of sulphate of ammonia in the counties of Cornwall, Devonshire, Somerset, and in a number of Welsh counties, the Association arranged to pay part of the railway carriage from neighbouring centres of production, and a considerable quantity of sulphate of ammonia was sold in this way at a price which did not interfere with the sales of local producers. The committee regard the money spent in this way as a good advertisement for sulphate of ammonia.

Patriotic Root Crop Competition.—Prizes amounting to £250 have been offered this season for the best crops of roots, cabbages, and potatoes. 40,000 schedules advertising the competition have been printed and are now in course of circulation. The results of last year's competition, which were highly satisfactory and formed an excellent advertisement, were published in the illustrated pamphlet "Luxurious Growth."

Scotland.—The propaganda work in Scotland continues to be carried out by Mr. J. D. Young under the direction of the Sub Committee composed of the Scottish Members of the Propaganda Committee. The Scottish Office issued a very effective illustrated pamphlet dealing with the results of the best of the 205 experiments laid down, 85 per cent of the trials being successful. Prize competitions have also been held on turnip crops, a total of 192 plots being entered. The results achieved were excellent and may be looked upon as valuable propaganda. A very effective exhibit was also arranged at the annual show promoted by the Scottish National Fat Stock Club at Edinburgh. Great interest was displayed in the Association's stand, the chief features of which were a display of farm and market garden produce and photographs illustrative of the season's field trials and of the process of manufacture of sulphate of ammonia. The photographs were by request presented to the Edinburgh and East of Scotland College of Agriculture to form the basis of lectures and demonstrations. The rest of the work in Scotland has consisted in attendance at markets, distribution of literature and advertising, the total outlay amounting to £1581.

Ireland.—Propaganda work has been carried out under the supervision of Mr. J. Irwin, and the successful results obtained from experiments in that country have been published in "Luxurious Growth." In view of the special arrangements made for home sales in England and Scotland, the Association received a very large number of enquiries from Irish merchants. The total sales to Ireland amounted to 750 tons, a considerable portion of this quantity being in lots of under 10 tons.

Staff.—Of the district supervisors, Messrs. Mosscrop, McEwan, Cattell, and Ettle have joined the forces. Messrs. Chandler, Falconer, and Hooper May are leaving the Association's service in September. Messrs. Blackhurst and Coates have obtained exemption from military duties and their services will be utilised in developing the commercial work of the Association among corn factors and manure merchants.

Overseas Propaganda.—Inquiries have been made with a view to commencing operations in India, Australia, the Argentine, and the Malay States, but owing to the difficulty in obtaining suitable men to supervise the experiments at the present time no definite steps have been taken. In Spain the propaganda work has been continued on a larger scale and sulphate of ammonia has been introduced into districts where it was unknown before. The sums expended on advertising have been increased and about 30,000 copies of pamphlets on various crops have been distributed. No experiments proper have been made, but a quantity of sulphate of ammonia has been parcelled out among small merchants in the new districts "on sale or return," the total expenditure under this heading amounting to £360, most of which we hope will be recovered. In Egypt the work has proceeded very satisfactorily under Mr. Georgiou's supervision. The Association has made an arrangement with Messrs. James Miller, Son, & Co., of Glasgow, with a view to providing a stock of sulphate of ammonia in that country until suitable local selling arrangements could be made. It is with pleasure that the committee report that over 1000 tons have been shipped under this arrangement, the demand for this being a direct result of our propaganda work. An arrangement has now been made between Messrs. Miller and The Egyptian Markets, Ltd., by which the extensive agricultural selling organisation of the latter will be available for the sale of British sulphate of ammonia in Egypt. The agreement contains a provision that The Egyptian Markets, Ltd., shall afford the Association every facility for the carrying on of propaganda work, and we have every hope that this arrangement will be of great benefit to the Association and lead to the permanent establishment of sulphate of ammonia in Egypt. Experiments and propaganda work have been carried out on a large scale and 25,000 copies of a pamphlet dealing with the manuring of maize and sugar-cane and containing the results of our successful Egyptian experiments are now being distributed in English, French, and Arabic.

Subscription.—The tonnage represented by subscriptions to the propaganda branch, viz., 325,447 tons, shows an increase of about 1500 tons, as compared with last year. To this must be added the production of several important manufacturers who have decided to join the Association as from July 1, 1916. The total tonnage of new members is 11,000 tons. We are very pleased to report that among the new members are the Bengal Iron and Steel Company, Ltd., the Metropolitan Gas Company of Melbourne, and Natal Ammonium, Ltd. According to our revised estimates, the quantity of sulphate of ammonia as such produced in the United Kingdom amounts to about 360,000 tons per annum, so that the Association is very nearly completely representative of British production. It is with deep regret that the Committee have to record the deaths of two of their colleagues, Mr. John Fyfe, of Young's Paraffin Light and Mineral Oil Company, Ltd., and Mr. W. J. D. Burnyeat, of the Cumberland Coal Owners' Association. Mr. Fyfe had been an active member of the Executive since the formation of the Sulphate of Ammonia Committee in 1897. Mr. Burnyeat joined the Executive on the formation of the Selling Committee.

It is also to be regretted that the Committee no longer enjoy the co-operation of Mr. Blumer, who has retired from Messrs. Bolckow Vaughan & Co., Ltd.

Messrs. Wood, Drew, & Co. offer themselves for re-election as auditors to the Association.

D. Milne Watson, *Chairman.*

84, Horseferry Road, Westminster,
July 17, 1916.

THE QUANTITATIVE DETERMINATION OF SILICA.*

By VICTOR LENHER and EMIL TRUOG.

The conventional method of attack of silicates in general consists in the sodium carbonate fusion, the treatment of this fusion with hydrochloric acid for the purpose of separating out the silicic acid, and the subsequent evaporation for the purpose of dehydrating this silicic acid and rendering the silica insoluble in water and in dilute hydrochloric acid. This method of separating silica from the bases has received a great deal of study, yet the results obtained are not all that might be desired. There is considerable uncertainty regarding the necessary length of time and temperature of dehydration, the need of repeated evaporation, the solubility of silica in acids and in the wash solutions used, and the presence of ferric oxide, alumina, lime, magnesia, potash, and soda in the non-volatile residue which remains when the weight of the silica is obtained by its loss when treated with hydrofluoric and sulphuric acids. The present investigation was undertaken for the purpose of studying the various errors in the determination of silica with the view of making the determination more accurate and if possible more expeditious.

Fresenius (*Quant. Chem. Anal.*, 1904, i., 510) states that direct heating over the lamp is not advisable, as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to form compounds which are not decomposed, or only imperfectly, by hydrochloric acid.

Gilbert (*Tech. Quart.*, 1890, iii., 61) investigated the effect of different temperatures of dehydration and the presence of considerable calcium and magnesium on the solubility and contamination of the silica. He worked with several furnace slags and orthoclase felspar. His conclusion may be summarised as follows:—Tempera tures of dehydration above that of the water-bath do not give much higher results for silica, but may increase the impurities in the silica considerably. These impurities cannot be removed by digestion for one hour with strong acid. Calcium and aluminium have no tendency to form silicates even at temperatures up to 280°. When magnesia is present the best results are obtained by dehydrating at 120°. Higher temperatures may cause the formation of partially soluble magnesium silicate.

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* From the *Journal of the American Chemical Society*, xviii. No. 5.

Hillebrand (*Journ. Am. Chem. Soc.*, 1902, xxiv., 362) furnishes data showing that the silica recovered with alumina and other oxides may again be partially lost, due to its increased solubility after the pyrosulphate fusion. This he states is an added argument in favour of recovering all of the silica at the outset, since the expectation of recovering all of what remains is based on an erroneous assumption. Because of this he states that Gilbert's results lose much of their value. If this criticism be accepted Gilbert's results still show that high temperatures of dehydration increase the impurities in the silica, and that the presence of considerable magnesia tends much more than lime and alumina to still further increase the impurities, besides causing more silica to go into the solution.

Bloor (*Ibid.*, 1907, xxix., 1603) in the analyses of clays made special note of the residues left after volatilisation of the silica, and found lime and magnesia present in amounts ranging from practically nothing to about 2 mgrms. of each. The dehydration was made on a water-bath. The total residues averaged about 1 per cent of the separated silica. When the dehydration temperature was raised to 125° the residues were greater, due largely to an increase of lime and magnesia. As possible reasons for the presence of lime and magnesia in the residues Bloor gives as the causes of error insufficient washing, incomplete decomposition at the outset, contamination from porcelain, and different deportment of clay and rock powder in the fusion.

Hillebrand (U.S. Geol. Survey, *Bull.* 422, 97, 1910) states that he has tested the residues carefully for lime and magnesia, and finds none of the former present and from nothing to 0·2—0·3 mgrm. of the latter.

Gooch (*Am. Journ. Sci.*, 1913, clxxxvi, 598), Reckert, and Kuzirian indicate that the main source of trouble in bringing precipitated silica to constant weight is not due to the presence of water but to impurities which are partially volatile. They also indicate that the impurities may consist in part of sodium chloride, which on heating with the blast lamp gradually loses chlorine and produces sodium silicate.

Bauer (*Tonind. Zeit.*, 1913, xxxvii., 89) states that silica may hold hydrochloric acid so strongly that a blast flame will not drive it off. He does not state whether the silica used was free from bases or salts, and hence the presence of chlorides is not precluded, and his contention correspondingly loses weight.

Wunder (*Ann. Chim. Anal.*, 1914, xix., 45) and Suleimann present results which show that the solubility of precipitated silica increases with the strength of hydrochloric acid used and also with the temperature of digestion.

Hillebrand (U.S. Geol. Survey, *Bull.* 422, 92, 1910) states that hydrochloric acid has a marked solvent action on the silica that is obtained in the usual analysis. He states that the use of dilute hydrochloric acid in place of water for washing gave unfavourable results.

Experimental.

Temperature of Dehydration.—Undoubtedly the more complete the dehydration the more insoluble does the silica become to the subsequent acid treatment. The completeness of dehydration is, however, limited by the temperature at which the silica reacts with the chlorides and the time which is permissible to use. The writers have been unable to find in the literature any report of a systematic investigation regarding this reversion temperature at which the bases, especially magnesia, start to combine with silica to a material degree. For the purpose of determining this the following experiments were carried out, in which only materials of known composition and high state of purity were used in order that the conditions could be controlled properly.

Materials Used.—Practically all of the silica on the market contains various bases as impurities; therefore silica of a high degree of purity was prepared as follows:—Silicon tetrafluoride was evolved by the action of sulphuric acid on a mixture of powdered quartz and calcium fluoride. From the generating flask the gas was conducted through a rubber funnel into water contained in a paraffined beaker. The gelatinous silica which separated out was filtered off, and after thorough washing was heated in a platinum dish with sulphuric acid until copious fumes of sulphur trioxide came off for ten minutes. This was done to drive out the last traces of hydrofluoric acid from the silica. The silica was then washed with pure water and strongly ignited. A 0·5 grm. sample of this silica left no weighable residue when treated with hydrofluoric and sulphuric acids and evaporated; hence was considered pure.

A second preparation was made as follows:—Pure silicon tetrachloride was dropped into water. After evaporating to dryness, which converted the gelatinous silica which had separated out to the granular form, the material was powdered and treated with sulphuric acid and thoroughly washed in the same way as the silica obtained by decomposing the fluoride. On evaporating a 0·5 grm. sample with hydrofluoric and sulphuric acids a residue of 0·05 mgrm. was obtained, which is within the limits of error of working. This silica was therefore as pure as that prepared from the tetrafluoride. When the silica from the tetrachloride was not treated with sulphuric acid it contained more impurities. Iron appeared to be the main impurity, and the conversion to the sulphate made its removal by washing possible.

Silica prepared from the tetrafluoride is very light and voluminous, making it difficult to handle and weigh. That prepared from the tetrachloride is more like ground quartz and hence is readily handled.

The hydrofluoric acid used was prepared by redistilling pure commercial acid in a platinum still. A 50 grm. sample left no weighable residue on evaporation and ignition.

The supply of sulphuric acid on hand gave on evaporation and ignition a residue of 0·0002 per cent, and hence was sufficiently pure.

The hydrochloric acid used was prepared both by redistilling pure acid, in which case the first and last portions were discarded, and by the action of sulphuric acid on sodium chloride, using appropriate wash bottles.

The other chemicals employed showed by blank tests or otherwise that they were sufficiently pure for the purposes intended.

Analytical Methods.—In our experiments 0·5 grm. samples of silica were always used. To the weighed sample were added the various amounts of calcium, magnesium, or ferric oxides, and from four to six parts of sodium carbonate. The amount of sodium carbonate used was regulated according to the amount of basic oxide added. The materials were mixed in a platinum crucible and heated by means of a burner until the fusion was quiet. The fused mass was then transferred to a platinum dish and treated with an excess of dilute hydrochloric acid (sp. gr. 1·05). After all but the silica had dissolved the solution was evaporated to dryness on the water-bath and the residue further heated for two hours at the temperature indicated in each series of experiments. After dehydration the mass was treated with 25 cc. of hydrochloric acid (sp. gr. 1·1). The dish was covered and digested on the water-bath for ten to twenty minutes. Any lumps appearing were broken up, and after diluting with water the solution was filtered. The silica was washed with water till the runnings no longer gave a turbidity with silver nitrate. This gave a filtrate of 200 to

300 cc. The silicate was volatilised in a weighed platinum crucible after the addition of a few drops of sulphuric acid and about 3 cc. of hydrofluoric acid. The residue was ignited and the crucible and contents weighed.

Two double-walled drying ovens, one of copper and one of sheet iron, were first used in the dehydrations. They were heated by two Bunsen burners. On testing these ovens carefully it was found that under the best conditions the temperature at various points on the same shelf in the oven varied as much as 10° and sometimes even more. The ovens were in good condition and the burners were carefully regulated. With less care and the use of two shelves thermometers variously placed would show a difference of as much as 20° in different parts of the same oven. The experiments with lime and with magnesia given in Table I. were carried out in these ovens. In all of the other experiments, except when a temperature higher than 120° was required, an automatic electric oven was used, which made it possible to control the temperature to which the dishes were heated to within 1°.

In Table I. are given the results when various amounts of calcium, magnesium, and ferric oxides were fused with silica and sodium carbonate, and where a dehydration temperature of 110° was used. From these data it is evident that lime does not seriously contaminate the silica at this temperature. With the large amounts of magnesia there are indications of contamination, but this is undoubtedly due to the poor regulation of temperature secured with the gas-heated oven, as already explained. The results with magnesia given in Table II. entirely confirm this probability. The ferric oxide contaminated the silica in all cases in an irregular way.

Table I.—*Non-volatile Residues Using Various Amounts of Basic Oxides.*

Dehydration Temperature, 110°.

SiO_2. Grm.	Na_2CO_3. Grms.	CaO. Grm.	N. V. R. Grm.
0·5000	2	0·0000	+0·0001
0·5000	2	0·0000	−0·0001
0·5000	2	0·0010	−0·0001
0·5000	2	0·0010	−0·0001
0·5000	2	0·0100	+0·0001
0·5000	2	0·0100	+0·0001
0·5000	2	0·0500	+0·0001
0·5000	2	0.0500	—
0·5000	2	0·1000	+0·0001
0·5000	2	0·1000	+0·0001
0·5000	4	0·2000	+0·0002
0·5000	4	0·2000	—
0·5000	6	0·5000	—
0·5000	6	0·5000	−0·0003

SiO_2. Grm.	Na_2CO_3. Grms.	MgO. Grm.	N. V. R. Grm.
0·5000	2	0·0010	−0·0001
0·5000	2	0·0010	—
0·5000	2	0·0100	—
0·5000	2	0·0100	—
0·5000	2	0·5000	+0·0002
0·5000	2	0·5000	+0·0002
0·5000	2	0·1000	+0·0005
0·5000	2	0·1000	+0·0001
0·5000	4	0·2000	+0·0003
0·5000	4	0·2000	+0.0002
0·5000	6	0·5000	+0·0003
0·5000	6	0·5000	+0·0001
0·5000	2·5	0·0100	+0·0009
0·5000	2·5	0·0100	+0·0005
0·5000	2·5	0·0500	+0·0021
0·5000	2·5	0·0500	+0·0028
0·5000	2·5	0·2000	+0·0005
0·5000	2·5	0·2000	+0·0019
0·5000	5·0	0·5000	+0·0012
0·5000	5·0	0·5000	+0·0009

Table II.—*Non-volatile Residues under Different Temperatures of Dehydration.*

Temperature.	SiO_2. Grm.	Na_2CO_3. Grms.	CaO. Grm.	N. V. R. Grm.
110	0·5000	2	0·1000	+0·0001
110	0·5000	2	0·1000	+0·0001
115	0·5000	2	0·1000	—
115	0·5000	2	0·1000	—
120	0·5000	2·5	0·1000	+0·0002
120	0·5000	2·5	0·1000	+0·0002
150	0·5000	2	0·1000	+0·0003
150	0·5000	2	0·1000	+0·0004
175	0·5000	2·5	0·1000	+0·0003
175	0·5000	2·5	0·1000	+0·0004
			Fe_2O_3.	
110	0·5000	2·5	0·0500	+0·0021
110	0·5000	2·5	0·0500	+0·0028
120	0·5000	2·5	0·0500	+0·0004
120	0·5000	2·5	0·0500	+0·0004
150	0·5000	2·5	0·0500	+0·0015
150	0·5000	2·5	0·0500	+0·0013
Temperature.	SiO_2. Grm.	Na_2CO_3 Grms.	MgO. Grm.	N. V. R. Grm
105°	0·5000	2·5	0·1000	+0·0001
110	0·5000	2·5	0·1000	+0·0001
110	0·5000	2·5	0·1000	+0·0001
115	0·5000	2·5	0·1000	+0·0002
115	0·5000	2·5	0·1000	+0·0006
120	0·5000	2·5	0·1000	+0·0010
120	0·5000	2·5	0·1000	+0·0012
150	0·5000	2·5	0·1000	+0·0008
150	0·5000	2.5	0·1000	+0·0018
175	0·5000	2·5	0·1000	+0·0007
175	0·5000	2·5	0·1000	+0·0011
Free flame	0·5000	2·5	0·1000	+0·0008
„	0·5000	2·5	0·1000	+0·0016

Table II. shows the results obtained when the amount of basic oxide added was constant (0·1 grm.) and the temperature of dehydration varied. From these data it is evident that lime does not seriously contaminate the silica unless the temperature of dehydration is at least over 115°. With magnesia the point at which the silica becomes contaminated with magnesia is reached at 115°. At 110° there is no appreciable contamination, which shows that the slight contamination of magnesia reported in Table I. was probably due to the poor regulation of temperature secured with the gas-heated ovens.

Ferric oxide contaminates the silica in an entirely irregular way at all temperatures, which suggests that it may be due to physical causes. Undoubtedly on evaporation and dehydration the ferric chloride by hydrolysis changes partly to oxide and oxychloride, which because of their lesser solubility are not as readily removed from the interior of the dried silica as calcium chloride.

Potash and soda have been repeatedly tested for in many experiments, but in our work have never been detected in the non-volatile residue. This is in accord with the work of Hillebrand (*Journ. Am. Chem. Soc.*, 1902, xxiv., 373) but not with the observations of Kuzirian (*Am. Journ. Sci.*, 1914, xxxvii., 61).

The general knowledge of the contamination of silica by the bases has been emphasised by those who have studied in detail the silica determination. It has been assumed by some that actual reversion to silicate takes place. It is not possible at the present time to state definitely just how these bases are retained by the silica. Hydrolysis alone will not account for the retention of lime or magnesia, since the products of the hydrolysis of calcium or magnesium chlorides are readily soluble in even dilute hydrochloric acid. The subsequent extraction with dilute acid should therefore remove the lime or magnesia, but such is not the case. In the case of contamination of the silica by iron, hydrolysis probably can be assumed to be at least one cause.

Adsorption might be advanced as a possible explanation but would hardly seem plausible. As a matter of fact the contamination is a very real thing and in the analysis of silicates always takes place. In the silica from basic rocks the non-volatile residue is usually very much higher than from those of acidic character.

It should be emphasised at this point that in the regular procedure of a silicate analysis, if the dehydrated silica and chlorides are treated first with water insoluble basic chloride of iron is formed, which will not completely dissolve in hydrochloric acid of any strength in any reasonable length of time. This is especially true when hot water is used. Sufficient hydrochloric acid, therefore, must be added to prevent this decomposition. On the other hand, large excess of hydrochloric acid must be avoided on account of its solvent action on the silica.

(To be continued).

SUBSTITUTION OF WOMEN IN INDUSTRY FOR ENLISTED MEN.

This is one of a series of notes relating to various industries which are being issued by the Government* with the object of making available for manufacturers all over the country the fullest information as to the processes in which and the methods by which temporary substitution of women for enlisted men is already being successfully carried out in their trade.

The Chemical Industries.

I.—*Processes in which Women can be substituted for Men.*

Substitution has begun to some extent in all the principal centres of the industry, but is more extended in some centres than in others, and at present is confined to a relatively small number of firms. Owing to the heavy nature of some of the work and to the fact that in the past it has been customary for the same man to be employed on different kinds of work, some too heavy for women, some comparatively light and suitable for women, a certain amount of reorganisation and adaptation will be necessary if women are to be substituted with success. In another respect the industry is exceptional, in that it affords scope for the employment of specially trained university women (chemists) in the works laboratories as analysts or research workers.

The following is a list of the processes in which women have under suitable conditions already been or can be successfully substituted for men:—

A.—*Alkali and Acid Manufacture.*

1. *Alkali.*—Emptying roll sulphur moulds. No substitution has been found in the process of alkali manufacture proper (but see Note 3, ii.).
2. *Acid.*—Filling, stoppering, and packing carboys. The adoption of women's labour in this work is facilitated by transport of the carboys on hand trucks. With moderate care the dangers of burning from sulphuric acid and of gassing from nitrous fumes in manipulating nitric or nitrous acid can be obviated.

See also under "C.—General Labouring Work" below.

B.—*Manufacture of Light Chemicals.*

1. *Use of Machines or Mechanical Apparatus.*—(*a*) Filter Press Work (Note 1):—
   - (i.). Scraping and cleaning ordinary filter presses. Suitability depends on the size and material of the press (women are being employed on 40-inch wooden and 37-inch iron presses).
   - (ii.). Screwing up, emptying, and cleaning gravity filter press.
   - (iii.). Working hydraulic press; for example, for compression of guncotton and for oil extracting. For this work a suitable working suit is desirable.

   (*b*) Centrifugals or Hydro-extractors.
   Loading, working, and emptying centrifugals (up to 50-inch cage diameter).

   (*c*) Electro-chemical Processes.
   - (i.). Refining and separation of metals. The adoption of women's labour to any great extent in this department, *e.g.*, in copper refining, depends on the size of the cells and on the use of lifting tackle when the anodes and cathodes are too heavy (Note 2).
   - (ii.). Feeding cells with solution.
   - (iii.). Removing deposit of precious metals from cells.
   - (iv.). Fitting cells with carbons and making plastic parts of cells.
   - (v.) Making cell luting.

   (*d*) Management of Stills.
   Supervision of water distillation plant.

   (*e*) Feeding or Working the following machines:—
   - (i.). Feeding only: — Disintegrator, mechanical siever, grinder, bucket elevator, edge runner.
   - (ii.). Working:—Band saw; using hand, over-head, lifting tackle (for moving drums up to one ton in weight).
2. *Manual Processes other than Warehouse Work.*
   - (*a*) Laboratory work, skilled and unskilled. Some trained chemists have been employed and unskilled workers are used for simple cleaning operations or for making routine tests.
   - (*b*) Emptying cooling or crystallising tanks (Note 3).
   - (*c*) Breaking up solid crystals (except large blocks requiring the use of a heavy pick or crowbar).
   - (*d*) Drying-cupboard work—
     - (i.). Conveying drying shelves or solids.
     - (ii.). Spreading out and raking over solids.
   - (*e*) Emptying subliming chambers.
   - (*f*) Stacking blue beds in white lead works performed in some factories prior to the war).
   - (*g*) (i.). Feeding and supervision of small boiling pans and of reaction vessels.
     (ii.). Supervision of evaporating tanks.
   - (*h*) Washing crystals in fine chemical works.
   - (*i*) Syphoning liquors into crystallising tanks.
3. *Warehouse Work.*
   - (*a*) Dry packing generally (Note 4).
   - (*b*) Wet packing (Note 4).
   - (*c*) Soldering tins and tin-paper linings of cases.
   - (*d*) Weighing and packing copper ingots.
   - (*e*) Storekeeping.
   - (*f*) Checking for dispatch.

C.—*General Labouring Work.*

1. —(*a*) Unloading boats and trucks of slack, coal, coke, firebricks, timber, sand, and drain pipes; (*b*) loading barges with coal, &c., and trucks with sacks.
2. Filling and wheeling barrows (loads up to 1½ to 2 cwt., including barrow).
3. Wheeling carboys of acids.
4. Washing, rolling, and painting iron drums.
5. Bagging coke, chemical manure, &c.
6. (*a*) Cleaning and emptying evaporating tanks; (*b*) general cleaning operations.
7. Trimming coal for furnaces and levelling ashes.
8. Washing bogies.
9. Breaking up pyrites.
10. Carting.

In addition women have been found in one or two cases employed in subsidiary trades ancillary to chemical works; *e.g.*:—

In Dry Cooperage — On a number of repetition machines;

In Basket Making;

In the Mechanics' Shop—In drilling, planing, screwing, and mortising.

Training.—The greater part of the operations performed require no special training or skill apart from careful instruction at the works in methods of tackling and of systematically arranging the work. Practice in hard manual labour and strict intelligent attention to instructions are chiefly necessary. In certain exceptional operations—for example, management of vacuum stills, long experience appears requisite for rapid appreciation and successful control of different combinations of causes which may affect the work, and which it is said to be almost impossible to schedule for the guidance of the new worker.

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* No. 17, Chemical Industries.

II.—*Supply of Women Workers and Type of Labour.*

Women of strong physique will be required for much of the work and intelligent women of a superior type for the more responsible work, and a careful selection of workers with reference to the particular class of operation is the primary condition of successful substitution. In London and other urban centres it may be necessary to recruit from a distance, and employers' attention is drawn to the special arrangements made by the Government for meeting such needs. Early application should be made to the local Labour Exchange by employers and the fullest possible information be given in order to secure the right type of woman. It is not anticipated that there will be any difficulty in securing the right type of workers if suitable arrangements are made and adequate remuneration offered.

III.—*Relaxation of the Factory Acts.*

In certain branches the necessity of carrying on the work continuously makes the introduction of women dependent on some relaxation of the law. Applications for such relaxations will be favourably considered by the Home Office where they are needed to facilitate production of supplies for the Crown, or to enable other work required in the national interest (*e.g.*, manufacture for export) to be carried out. Any such application should be addressed to the Inspector of Factories. The attention of employers is particularly directed to the arrangement found in certain parts of the country of working in eight-hour shifts, which appears specially suited for introduction of women's services.

IV.—*Arrangements in Factories.*

Special arrangements of a simple and practical character will be necessary to render the heavier and more dangerous work suitable for women. A good example of labour-saving arrangements in connection with the loading and unloading of trucks is the erection of rough platforms with access by planks on a gentle incline, which have been found of great service. Other mechanical appliances, such as arrangements for "blowing over" liquors instead of carrying by hand; introduction of lifting tackle where heavy plates, &c., have to be lifted, and of lighter implements (barrows, pulleys, spades, &c.); and the provision of suitable protective clothing for wet, dangerous, and dirty processes, have facilitated introduction of women. It should be kept in mind that care on the part of employers to secure the welfare of women brought in will greatly increase the probability of their employment proving successful.

The district inspectors and lady inspectors of factories are ready to advise and assist employers in regard to any questions of safety, health, and welfare that may arise in the works. The assistance of Labour Exchange officers and the local advisory committees on Women's War Employment (where appointed) may be invoked in case of special requirements in regard to lodging and transit of imported workers or other local welfare problems.

Notes.

1. In addition to the processes named inspectors have found women learning to manipulate the pump or valve regulating the flow of liquor.

2. The inspectors consider that women could satisfactorily be employed to a greater extent than has been yet attempted on the management of cells.

3. (i.). Women have been found employed on coolers (or crystallising tanks) 5 ft. 6 in. deep. Two women emptied and one carried away. A strong type of woman is essential. In one instance women dug out tanks barefoot, in another they wore clogs or boots. One cooler, containing over two tons of material, would be emptied daily. Women have been employed on borax coolers for years and are considered satisfactory. (ii.). It is desired to call the attention of employers to the possibility of employing women on the analogous operation of emptying sulphur tanks in the Chance recovery process, in which the work is certainly less arduous than that involved in the above case.

4. Technical difficulty in employing new labour on these processes in fine pharmaceutical chemical manufacture can be and has been met by a simple check system, by which the worker relies solely on numbers and is not assumed to have any specific technical knowledge.

(Copies of this pamphlet can be obtained on application to the District Inspector of Factories, or to the local Labour Exchange Manager, or to the Employment Department, Board of Trade, Queen's Anne's Chambers, London, S.W.).

LIEBIG'S EXTRACT OF MEAT CO., LTD.

At the Fifty-first Ordinary General Meeting of the above Company, held at Cannon Street Hotel, on Wednesday, August 2, the Chairman stated that during the period under review the Company had completed fifty years of trading, and it was with no little pride that they looked back upon the great developments that have taken place since then of the industries in which the Company was the pioneer, and particularly upon the growth and success of their own business. The progress since those early days of the River Plate, of the railways there, and of the pastoral and agricultural industries, hah led to appreciation of cattle and land, and the Company had shared in that prosperity by reason of the extensive organisation of cattle farms which they had acquired.

The turnover during the year had been a large one, and prices had been satisfactory, so that notwithstanding the high cost of materials, of coal, and the extraordinary high rates of freight the result of the year's trading had been good.

The Company had recently introduced various new administrative measures in regard to the working and development of their estancias which they believe will be productive of good results.

During part of the year Mr. R. B. Cunninghame-Graham, the head of the British Remount Commission in Uruguay, and his staff continued to make Fray Bentos their headquarters for the collection of remounts.

Speaking about the River Plate in general, the Chairman mentioned that at the outbreak of the European war, the country was in the midst of a severe crisis, but that conditions now appear to be gradually and steadily improving, no doubt largely due to the Allies' purchases of beef, grain, &c., and he thought there was little doubt but that the River Plate countries would be among the first to enter upon a fresh period of prosperity when the war is over.

As regards the ranches of Rhodesia, matters are proceeding normally, the Company have a nucleus herd of over 20,000 head of cattle which are being graded up by the importation from time to time of Sussex and Aberdeen Angus bulls and heifers, the first cross calves of both these strains showing marked superiority in weight over the native cattle, while they appear at the same time to be not inferior in hardiness.

On the motion of Mr. Arthur Woods, seconded by Dr. H. M. Boker, 500 guineas was voted to the funds of the British Red Cross Society and the Order of St. John of Jerusalem, and the final dividend of 10 per cent (making 20 per cent for the year), and bonus of 5 per cent, all free of income tax, were confirmed.

THE CHEMICAL NEWS

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THE FRUIT OF *VACCINUM CORYMBOSUM*.

By CHARLES H. HARRIS and WILLARD D. THRAMS.

The fruit, which consists of clusters of berries, were gathered near the sandy shores of Oneida Lake at Sylvan Beach, New York, August 1—10, 1915. It is the common swamp blueberry, usually called huckelberry outside of New England. The fruit grows abundantly on shrubs six to ten feet in height and is dark blue in colour. It was dried in an oven until practically constant weight was attained. The dried berries averaged 0·0555 of a grm. in weight, and each contains 12 to 15 small nutlets. The fruit is an important article of food and is widely used.

The Ash.—The ash constituents were determined from six different portions of 2 grms. each. These were burned in a weighed platinum dish. From the first portion silica, iron, alumina, calcium, and magnesium were determined; from the second sodium and potassium; from the third the sulphate; from the fourth the phosphate; from the fifth manganese. In burning the fruit gives off a peculiar sweetish odour. The results were as follows:—

SiO_2	6·33	per cent	of the ash
Al_2O_3	17·39	„	„
Fe_2O_3	10·50	„	„
CaO	18·11	„	„
MgO	11·48	„	„
K_2O	5·65	„	„
Na_2O	2·26	„	„
SO_3	10·94	„	„
P_2O_5..	14·36	„	„
MnO	0·35	„	„
Cr	—	„	„
Total ..	97·37	„	„

There was a small amount of CO_2 which we did not determine. The ash is 1·38 per cent of the dried fruit.

Proteins.—We heated some of the fruit in a test-tube with soda lime, and observed the odour of ammonia. The nitrogen was determined by the Kjeldahl-Gunning method and found to be 0·7 per cent of the dried fruit.

The Sugars.—We placed 50 grms. of the dried fruit in a 500 cc. flask, fitted with an inverted condenser. It was treated with 95 per cent alcohol for twenty weeks, until a test with Febling's solution showed only a trace of sugar. After distilling off the alcohol the residue was a dark heavy syrup. Acetic acid fermentation soon commenced, as indicated by the odour. The last traces of sugar were removed by treating for a few weeks with water.

A portion of the sugar solution was digested on the warm water-bath several hours with bone-black to remove the colour. The solution, however, continued a light brown colour. The alcohol and water extracts were both treated with standard Fehling's solution. We found 38·50 per cent sugar in the alcoholic extract and 2·96 per cent in the water extract, a total of 41·46 per cent. Testing further with phenylhydrazine showed the sugar to be fructose.

The Acids.—The acid tests were made from the alcohol and water extractions. Tartaric acid and a trace of citric acid were found. The acetic acid present was due to the fermentation of the sugar.

The Oils.—We removed the sugars from 400 grms. of fruit by the method outlined, and dried the residue, which weighed 103 grms. This was finely ground, and placed in a half litre flask fitted with a reflux condenser. It was treated with ether for about ten weeks before all the oil was removed. It was of a dark straw colour and sweetish taste. We obtained 3·75 grms. of oil, or 0·93 per cent of the dried fruit. The specific gravity at 18° C. is 0·9.

A small amount, about 1 grm., was saponified by the Koetstorfer method, and the saponification equivalent was found to be 350·96. Two other determinations gave concordant results. This number with the specific gravity agrees quite closely with rape seed oil. Saponification took place in a comparatively short time.

We desire to express our thanks to Dr. N. Knight for assistance in this work.

Cornell College. July 6, 1916.

PINK COLOUR ON THE SURFACE OF FATS.

By ARTHUR W. KNAPP, B.Sc., F.I.C.

Many analysts must have noticed that when beakers of margarine fat are left about in the laboratory the surface becomes red or pink. The colour appears to spread from centres, and is generally produced where the surface shows crystalline structure. The appearance suggests bacterial growth, but experiments show that the colour can be produced in sterile fat without inoculation. It was found that the colour was not produced when the margarine was placed in a drawer in the dark, or if the sample were placed in a desiccator containing alkaline potassium pyrogallate. From this it was concluded quite incorrectly that light and oxygen were essential. This suggested that the change might be due to the development of rancidity. But neither fatty acids nor rancid fats give the pink colour when added to margarine.

Fats which became pink were found to be artificially coloured. The yellow colour present is an azo dye (and most probably di-methyl-amido-azo-benzene or "butter yellow"). Further experiments showed that when this colour was present in fat it was not affected by carbon dioxide or fatty acids, but was readily changed to red by *vapour* of mineral acids. If the colour is due to the acid ion, it is curious that the colour should be ionised by hydrochloric acid when dissolved in fat. A filter-paper or a fat coloured with an etherial solution of "butter yellow" is very sensitive to acid and alkaline vapours. I conclude that the red colour which is developed on the surface of margarine is due to the mineral acid vapours in the air of the laboratory acting on an azo dye in the fat. As "butter yellow" might be used to colour either butter or margarine, the development of the red colour does not serve as a distinction. However, as most margarines give the colour, whilst few butters give it, it is evident that azo dyes are more frequently used in margarine than butter. As a method of detecting azo-dyes, the test should be carried out as follows:—

The filtered fat is run into a small beaker, allowed to solidify, and a number of such beakers placed in a crystallising dish, on the bottom of which is a filter-paper soaked in strong hydrochloric acid. They should be covered up and left thus for two hours and then examined. The fat should be free from water and curd, as the unfiltered fats give much less decisive results, the curd being darkened by the action of the hydrochloric acid. The pink colour is first seen on the surface, but soon a coloured layer appears. It is worthy of note that the hydrochloric acid gradually diffuses into the fat, and the rate of its diffusion may be measured by the growth of the red layer. In one experiment with butter-fat containing 0·01 per cent of the azo colour it penetrated 1/16th inch in one day, ½ inch in ten days, and 2 inches in forty-nine days.

It is not impossible that the study of the diffusion of vapours and gases into fats would throw light on the problem of rancidity.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Rock Lichen (*Parmelia saxatilis*).—This specimen of cryptogamic vegetation spreads out profusely in suitable localities over sheep-walls, withered barks of trees, &c., and is a sufficiently good representative of the class to which it belongs. The chemistry of lichens is difficult and rather confused, because it is not easy to separate and purify the constituents extracted by solvents, and besides these constituents are liable to vary in amount and to be subject to decomposition and hence to be contaminated by the products thereof. The dried plant gathered on October 22 yielded to boiling benzene 0·8 per cent of a brownish yellow extract which consisted of a white waxy matter belonging to the fatty series and mixed with some ergosterine. Boiling alcohol yielded a crystalline deposit on cooling as well as on adding water, and the liquid gave with $FeCl_3$ a violet colour, with bleaching lime solution a transient red, and with dilute alkalis a yellow passing to purplish brown colour, but on adding HCl a red-brown precipitate gradually formed; there was no tannin or sugar. The hot aqueous extract gave nitrate and much the same reactions, but the subsequent extract by dilute soda gave a very deeply tinted rust-brown liquid, which on adding acid gave a voluminous granular precipitate and a clear colourless liquid. A small quantity of pentosan and some polysaccharide (lichenin), but no starch, galactan, or oxalate were obtained. The ash amounted to 5·4 per cent and contained 13·3 per cent soluble salts, 5·5 silica and earthy matter, 2·8 CaO, 1 8 MgO, about 20 oxides of iron and manganese, 4·1 P_2O_5, and 1·1 SO_3. An aqueous extract of the fresh lichen on February 2 contained a considerable amount of nitrate, much gummy matter, and a quantity of the dyeing substance sufficient for recognition; the solution on addition of vanadate of ammonium slowly turned a bright yellow; it reduced Nessler's reagent to metal, but not $AgNO_3$, and on adding a little soda, boiling, and adding chloroform, a reddish yellow fluorescence was observed in reflected light. The constituent yielding these reactions has been called lobaric, usnetic, stereocaulic, and saxatilic acid, $C_{19}H_{14}O_{10}$, is white and very bitter, and a derivative of orcinol; on boiling layers of the lichen with a layer of wool for four hours the wool is directly dyed a clear russet-brown, extremely permanent. The underside of the plant is of a dark brown shade, which is said to be due to the action on the acid of the potash derived from the weathering of the rock on which the lichen grows. This product, however, is insoluble in water, whereas the dye is soluble and hence less oxidised or dehydrated. I have already (Chemical News, 1912, cv., 25) endeavoured to explain the origin of these very peculiar lichen acids by reference to the symbiotic association of algæ and fungus occurring in the lichen plant, but it would appear that the process of the formation of these acids is not so simple or direct as that of tannins and other chromogens of the higher plants. It may be that the nuclei of orcinol or anthracene from which they are derived are not originally present in the molecule of the protein substance of the fungal constituent, and that they arise only by a subsequent transformation of some other nuclei after these have been methylated by the plant. The especial frequency of lactone acids and methyl esters, their bitter taste, insolubility in water, optical activity, their appearance as excretions on the cell walls both of the vegetative and the reproductive organs at all periods of the year or at any latitude, &c.—all these properties recall to a great extent those of the bitter principles of the higher plants. The copious and ample intercellular spaces of the lichen supply the conditions of a very intense process of deassimilation (oxidation), which results in some cases in the production of chromogenic groups of very powerful reactivity—facts which indicate that an abundant overflow of nitrogenous matters is much in request not only for the gonidia, but also for the fructification on the epithallus. Not one of the lichen acids are coloured blue or green; but some of them, lecanoric acid especially, may by artificial treatment produce a red substance (litmus), which with ammonia yields a fairly good blue inclining to purple; but this effect is due to the addition of an inert nitrogen atom to the molecule, which atom serves to check the otherwise natural tendency of orcinol on higher oxidation to assume dark red or brown shades.

Primrose (*Primula vulgaris*).—This plant prefers a strong clay soil, and is partial to moorlands and to gravelly banks in shady woods and thickets. Its graceful form and its aspect of compact neatness quite free from anything blowsy or blatant have secured the special favour of all our great poets. Its particular systematic position in the world of plants, however, renders it an object of very great interest to the student of botanical chemistry. It is ranged among the gamopetalæ with superior ovary and usually regular flowers, but its chemical constituents vary widely from those of the majority of this type of organism. An analysis of the leaves was made at various periods, that of May 10 yielding to boiling benzene 2·6 per cent of a white pasty wax (pseudo-stearoptene), with no glyceride and very little carotin; boiling alcohol withdrew from the residue of the leaves a little flavone which was not a quercetin glucoside, also much chlorophyll and some saponin of a whitish granular consistence; there was also much pectosic mucilage, little or no sugar, and no reserve starch. The ash of the dried leaves amounted to 14·9 per cent and contained 61·9 per cent soluble salts, 6·3 silica, 12·2 CaO, 3·4 MgO, 4·2 P_2O_5, 4·3 SO_3, 17·2 Cl, about 5 oxides of Fe and Mn, and 12 CO_2. On June 20 they had a little catechol tannin. On November 3 leaves got in a dark shady wood had a little tannoid which fused with potass gave phloroglucol only apparently, also they had some oxalate of calcium. On December 26 they contained nitrate and a little sucrose, also a flavone which yielded no quercetin and seemed to have a para group; there was also pectosic mucilage and a little pentosan. Thus it would appear that in these radical leaves closely connected with the rhizome the physiological processes are not intense, the reason being no doubt that owing to their situation they are not greatly utilised as sources of supply for the organic needs of other parts of the organism. The flowers yielded 1·7 per cent of wax and carotin with a little resin, but no glyceride; they also contain a flavone which seems to be luteolin and not quercitrin, a little catechol tannin, some saponin, glucose, and oxalate of calcium together with much pectosic mucilage. The flower shaft has a good deal of tannin, and its red pigment is due to the deassimilation induced by the nitrogenous demands of the very numerous ovules which manifest a specially intense vitality. The long stout finely branched roots dug up on January 27 contained nitrate, sucrose, a little glucose and malic acid, some pectosic mucilage and pentosan, also cyclamin which responded to saponin tests very clearly; it dissolved in sulphuric acid with a fine pinky red coloration passing to a permanent violet; the cells of the cortex of these roots are packed full of large spindle-shaped granules of starch; there was no tannin, alkaloid, or oxalate. I do not contend that these starch granules were originally formed in the leaves; they were formed on the spot. The genus Primula is of a rather inferior organisation, many of its species have no well defined characters, so that their classification is difficult. Perhaps the conditions of their growth and requirements as regards soil, situation, and nutriment may account for this lacking in fixity. With a strong transpiration and a tendency to produce glandular hairs, internal secretory glands, passages, &c., there is little or none of that fixation of chemical products in the ordinary cells which indicates a decrease or absence of plastic elements. In fact, this genus by the great variability of its vegetative organs is distinguished by the plasticity of its protoplasm. The long pedicel or peduncle and the radical leaves ensure a strong development of anthocyan in the corolla, which in its lower parts (tube) is more robustly constituted than in its upper parts (limb). and hence it happens that the central area of the flower is tinged by carotin, and in some species, varieties, or hybrids the carotin granules are intermingled in the cell sap with the anthocyan of the entire corolla, and thus in this organ there occurs a kind of struggle between the rival processes of assimilation and deassimilation.

Dock (*Rumex sanguineus, &c*).—The study of these plants cannot be neglected by the botanical chemist, inasmuch as phenomena of great importance are presented, and questions of general interest are opened up in the course of their analysis. Their systematic position is not clear, and so they have been huddled up among the incomplete division of the class Dioctyledones. The leaf-blades taken on August 1 and dried yielded 2 per cent of a mixture of much wax and carotin with no glyceride. The alcoholic extract contained quercitrin and much tannin, which very clearly indicated the presence therein of a phloroglucol nucleus, and not easily oxidised to gallic acid. There was only a little sugar or starch, but much nitrate, pectosic mucilage, and oxalate of calcium, especially in the epidermis; the crude fibre amounted to about 50 per cent. The ash of the dried leaves and petioles attained 11·7 per cent and yielded 46·3 per cent soluble salts, 7·3 silica, 17·5 CaO, 5·3 MgO, 5·8 oxides of Fe and Mn, 6·2 P_2O_5, 3·3 SO_3, and 5·4 Cl; there was very much CO_2, over 20 per cent. The thick fleshy tap root blackish and clothed with filaments at the apex has no mycorhiza, and contains much nitrate even in winter, also much starch, mucilage, and pentosan, a good deal of catechol tannin, but little or no sugar or oxalate. The most interesting constituents are, however, certain anthracene derivatives, viz., according to Hesse, chrysophanic acid, nepodin (2 : 3 diethyl-anthracatechol), and lapodin (1 : 2 diethyl-anthragallol). The benzene extract of the dried powdered root was yellow and nearly all soluble in dilute soda; this solution precipitated by HCl, the precipitate washed and extracted with cold alcohol, the solution contained no ortho-quinone, and on evaporation to dryness was coloured fine red by H_2SO_4; the residue insoluble in alcohol was dissolved by boiling benzene, and evaporated dry gave no colour with carbonate of ammonium, a faint red with carbonate of sodium, and a splendid deep red with caustic soda. It would seem, therefore, that these anthraquinone derivatives are derived from the catechol nucleus and not from the phloroglucol nucleus of the phlobaphene of the tannin. If this be the case, the distinct and decisive phloroglucol reactions which this tannin yields are sufficiently accounted for. However, the powerful reactivity of these dock plants vividly recalls that of many species of the order Ericaceæ, but no anthraquinones are produced by the latter, their phlobaphenes not being so exposed or so prone to oxidation. In the dock tribe it will be observed that, although their foliage is generally abundant and well developed, their flowers are produced in great profusion, frequently appearing comparatively far down upon the stem. This provision would ensure an active and vigorous commotion in the physiological processes of the roots; the oxidation attendant on the formation of the aromatic compounds in those organs would be more intense and carried much further than what would ordinarily come to pass.

Daffodil (*Narcissus pseudo-narcissus*).—The host of golden daffodils that decorate the underwoods, copses, banks, &c., and follow close on the declining snowdrops in spring, are quite hardy, not particular as to soil, but thrive best on a deep cool soil partly shaded by trees. It is a slow growing plant with small transpiration and considerable absorptive power. Boiling benzene on the dried overground parts yielded 3·1 per cent of a mixture of wax, fat-oil, phytosterin, and a moderate quantity of carotin. Boiling alcohol extracted a distinctive amount of a quercetin flavone, also some sucrose and scillain, and a trace of alkaloidal matter apparently. Hot water, &c., withdrew much pectosic mucilage, a little reserve starch, some more sugar, a little pentosan, and oxalate of calcium precipitating in fine crystals. The ash of the leaves contained 61·4 per cent soluble salts, 3·3 silica, 10·1 CaO, 3·6 MgO, 5 P_2O_5, 4 SO_3, and 9·8 Cl, with considerable manganese; the carbonates were mostly soluble. One of the bulbs of Wordsworth's daffodils on the west shore of Ullswater was reverently extracted in early spring, and was found to contain starch, mucilage, inulin, alkaloid, and much oxalate of calcium appearing as raphides in the scales and roots. This alkaloid, which sometimes pervades the whole plant, is, according to Ewins (*Journ. Chem. Soc.*, 1910), very stable, is not similar in effect to atropine or pilocarpine, is $C_{16}H_{17}O_4N$ with no carbonyl or methoxy groups. It seems to be connected with or identical to scillain, although this glucoside has no nitrogen. The flowers contain a dark yellow-brown fat and much carotin tincturing chromoplasts of uniform colour and homogeneous structure; there is also a dissolved pigment which is quercetin; no volatile oil is obtained by distillation. According to the foregoing analysis it would appear that, owing to the great absorption of water and perhaps also the prevalence of acids in the sap, there is very little carbohydrate produced in the form of starch; it is only occasionally that a little starch appears around the lower portions of the vascular bundles of the leaves, while the chloroplasts are very scarce, the chlorophyll being confined to granules and fine masses thereof being impregnated with oil. It has been stated that a "plant with a bulb in which to store carbohydrates may rarely have sufficient concentration of sugar in the leaf to necessitate the formation and deposition of starch there," but it is difficult to see how this would affect the concentration of the protoplasm which induces the formation of starch. What the precise conditions are which lead to the production of starch in general do not seem to be clearly understood. The phenomenon cannot be explained in the final causeway, as Stahl has attempted. There is no doubt, however, that if too much moisture is absorbed the physiological powers of the plant are weakened, as potato stems for instance, with 90 per cent of water and its leaves with 85 per cent of water contain no starch; if, however. the potato flourished naturally on damp or marshy soils it would undoubtedly be prone to manufacture copious starch, as in that case its assimilatory powers would not be impaired, nor would its sap owing to the constant dilution by fresh water become specially acid. It would seem, therefore, that the absence or deficiency of starch in a leaf depends upon the retention of the water therein, whereby it tends to assume an acid reaction, and thus checks the process of assimilation so far as this carbohydrate is concerned.

Patterdale, Westmorland.

[With great regret we have to announce that the author of the above article died at Ullswater on Thursday, the 10th inst.—*Ed.* C.N.].

DETERMINATION OF VOLATILE THINNER IN OIL VARNISH.*

By E. W. BOUGHTON, Associate Chemist.

I. *Introduction.*

Almost all oil varnishes contain, as thinner, gum spirits of turpentine, "mineral spirits," or a mixture of the two. (In this paper the term "oil varnish" means varnish containing fixed oil and resin. The term "mineral spirits" is being generally accepted for the petroleum distillates that are used as substitutes for turpentine). Most of the turpentine substitutes prepared for use in paint and varnish are made from mineral oil. Benzene (C_6H_6), carbon disulphide, alcohol, and wood turpentine are very rarely used for oil varnish, though wood turpentine is frequently used in the manufacture of driers.

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* Technologic Papers of the Bureau of Standards, No. 76, Department of Commerce, S. W. Stratton, Director.

The definition for "volatile thinner," proposed by Committee D—1 of the American Society for Testing Materials, is as follows: "All that liquid portion of a paint, water excepted, which is volatile in a current of steam at atmospheric pressure" (*Proc. Amer. Soc. for Testing Materials*, 1914, xiv., I., 225).

II. *Purpose of Investigation.*

Since there has appeared no published work in which different methods for the determination of volatile thinner have been compared by the analysis of samples containing turpentine and of samples containing mineral spirits, this investigation was undertaken in order to ascertain the accuracy and convenience of the different methods.

III. *Review of the Literature.*

Mills (*Journ. Soc. Chem. Ind.*, 1886, v., 222) stated that the volatile portion of a varnish can be determined by "simple evaporation with water." McIlheney (*Journ. Am. Chem. Soc.*, 1894, xvi., 344) was the first to investigate the subject systematically, but all the samples that he analysed contained as thinner only turpentine. By direct distillation under reduced pressure he obtained results that were too low. By heating films of varnish at 100° C. for three-quarters to one hour he obtained results for percentages of volatile thinner which with two samples were very close to the amounts actually present and with a third sample were too low. By distilling off the turpentine from a 25-grm. sample of varnish with a current of steam, separating the water in the distillate from the turpentine and weighing the latter, he obtained satisfactory results. To correct his figures for the solubility of turpentine in water he added 0·3 grm. to the weight of the former. Approximately 100 cc. of water were condensed. He proposed this method for general use, stating that besides being accurate it has the advantage of leaving the non-volatile portion in a condition that is suitable for further examination. Livache and McIntosh ("Manufacture of Varnishes," 1911, iii., 184) quoted McIlheney and recommended his method. Walker (*Bull.* 109, revised, Bur. of Chem., Dept. of Agriculture, 1910) modified McIlheney's method by heating the still containing 100 grms. of the varnish at 130° C., adding to the weight of the volatile thinner 0·3 grm. for each 100 cc. of condensed water. Sabin ("German and American Varnish Making," 1912, 250) and Holley ("Analysis of Paint and Varnish Products," 1912, 23) recommended the latter method. Wolff (*Farben-Zeit.*, 1912, xvii., 849) stated that in the steam distillation heating the still containing the varnish at 110—115° C. is necessary for complete distillation of the thinner. Brown (*Proc. Amer. Soc. for Testing Materials*, 1914, xiv., 467) proposed a method for the determination of volatile thinner in insulating varnish, according to which 3 to 4 grms. of the sample are dissolved in ether (or some other readily volatile solvent), the solution diluted to 50 cc. in a graduated flask, and 10 cc. of the solution are flowed from a pipette upon a weighed glass plate with a ground surface. The plate is kept at room temperature and weighed at intervals until no further loss occurs. If the varnish contains a "very active drier" the plate is kept in a current of illuminating gas. Brown also determines the specific gravity of the varnish and of the thinner as obtained by distillation, and calculates the percentage by volume of thinner and "body" (non-volatile portion). He claims for his method the advantage that by continuing to weigh the plate at intervals one can determine the rate of oxidation of the film.

IV. *Experimental.*

1. *Collection and Preparation of Samples.* — Two samples of varnish were obtained from a reliable manufacturer, one being made from rosin, linseed oil, Chinese wood oil, driers, and "mineral spirits," and the other from a hard gum, hardened rosin, linseed oil, Chinese wood oil, driers, and turpentine. These samples are subsequently designated as A and B respectively. An examination of the distillate obtained from B showed that it contained a very small amount (about 2 per cent) of "mineral spirits." Two samples of varnish were prepared in the laboratory, the non-volatile portion of both consisting of approximately equal parts by weight of calcium resinate (prepared by heating rosin with 5 per cent of its weight of slaked lime) and boiled linseed oil (containing lead and manganese). In one case the thinner used was turpentine and in the other light mineral oil. These samples are designated as C and D respectively. Examination of the distillates obtained from A and B and of the thinners used to prepare C and D gave the results shown in Table I. The distillation was made with an Engler apparatus (T. B. Stillman, "Engineering Chemistry, 1897). The light mineral oil that was present in A and D is fairly representative of mineral-oil varnish thinners.

2. *Determination of Volatile Thinner by Different Methods.*—Four methods were used for the determination of the amounts of volatile thinner in A, B, C, and D.

Method 1.—A steam distillation was made, using 100 grms. of varnish, the still containing the varnish being heated to 115—120° C. in an air-bath. The distillation required from one and one-fourth to one and one-half hours and the volume of water condensed varied from 550 to 700 cc. The distillate from the varnish was separated from the water and weighed. The "corrected" results (see Table II.) were obtained by adding to the weight of the volatile thinner 0·3 grm. for each 100 cc. of water condensed.

Method 2.—Approximately 1·5 grm. of varnish were placed in a stoppered glass vial and the vial and contents weighed. The varnish was poured into a weighed metal dish, having a circular flat bottom 8 cm. in diameter; the stopper was replaced and the vial and stopper weighed. The dish was heated in an air-bath at 110—115 C. until no further loss in weight occurred. The maximum time required was three hours. The loss was assumed to be volatile thinner.

Method 3.—Brown's method. (See *ante*). With A and B a mixture of ether and chloroform was used, but C and D dissolved readily in ether. The films obtained were very uneven, being thickest at the edges of the plates. The plates were placed in a dust-free glass-walled cabinet with free access of air. The plates were weighed at intervals until no further loss occurred. The maximum time required was three hours. The loss was assumed to be volatile thinner.

Method 3*a*.—This was the same as Method 3, except that the plates were kept in a current of illuminating gas. The maximum time required was three hours.

Method 4.—A small stoppered vial, containing about 1 grm. of varnish and a small camel's-hair brush, were weighed together. The contents of the vial were poured upon a weighed glass plate, 10 by 15 cm., and brushed out to a thin film. The stoppered vial and brush were then weighed. The films of varnish weighed 0·6 to 0·9 grm. The plates were allowed to stand in the cabinet used for Method 3 and were weighed at intervals until no further loss occurred. The first weighing was made at the end of two hours and subsequent weighings showed that no further loss occurred in any case. The loss was assumed to be volatile thinner.

The temperature of the room during the determinations by Methods 3, 3a, and 4 varied from 30 – 35° C.

The results obtained by all methods are shown in Table II.

V. *Discussion of Results and Methods.*

The uncorrected results obtained by Method 1 and those obtained by Methods 3, 3a, and 4 are all as concordant as can be expected. It was also to be expected that slightly higher figures would be obtained by Method 3a than with Method 3. The percentages of volatile thinner in C and D obtained by Method 1 (uncorrected) and by Methods 2

Table I.—*Results of Examination of Thinners.*

Material.	Specific gravity at 15·6/15·6° C.	Refractive index at 20° C.	Unpolymerised residue. Per cent.	Refractive index of unpolymerised at 20° C.	Initial boiling-point. ° C.	90 per cent distilled at ° C.	95 p.c. distilled at ° C.
Distillate from A ..	0·763	1·423	—	—	119	175	187
Distillate from B ..	0·864	1·470	2·5	1·473	—	—	—
Thinner used for C. ..	0·869	1·471	1·2	1·513	—	—	—
Thinner used for D...	0·761	1·425	—	—	118	178	190

Table II.—*Results of Determination of Volatile Thinner by Different Methods.*

Method	Sample A, mineral spirits.		Sample B, turpentine.		Sample C, 50·1 per cent turpentine present.		Sample D, 53·9 per cent mineral spirits present.	
	Found. P.c.	Mean. P.c.	Found. P.c.	Mean. P.c.	Found. P.c.	Mean. P.c.	Found. P.c.	Mean. P.c.
No. 1	50·0 49·2 51·7	49·6	52·5 53·5 54·4	53·0	48·9 49·5 51·0	49·2	52·7 53·0 54·7	52·9
No. 1 (corrected)..	51·3	51·5	55·4	54·9	50·2	50·6	54·9	54·8
No. 2	49·1 49·6 48·7	49·4	52·9 52·7 51·8	52·8	50·0 49·2 49·3	49·6	53·3 52·3 53·4	52·8
No. 3	48·7 48·6	48·7	51·0 52·6	51·4	49·0 49·2	49·2	52·8 53·0	53·1
No. 3a	49·3 49·1	49·0	52·2 52·8	52·4	50·0 49·5	49·6	52·9 53·3	53·0
No. 4	49·1	49·1	52·6	52·7	49·6	49·6	53·4	53·4
Mean	—	49·5	—	52·9	—	49·6	—	53·3
Maximum deviation from mean	+2·2	+2·0	+2·5	+2·0	+1·4	+1·0	+1·6	+1·5
Maximum deviation from known..	—	—	—	—	−1·1	−0·9	−1·6	−1·1

3, 3a, and 4 are but slightly less than the amounts actually present, and the corrected results by Method 1 are but slightly greater. It appears, therefore, that for such varnishes the most convenient method may be selected for routine use. During the application of varnish the thinner is rapidly evaporating, so that for practical purposes an error of 1 per cent in the determination is of no significance. In this laboratory Method 2 is used, the result being reported as the whole percentage next above the figure obtained. Should the steam distillation method be used, with subsequent correction of results, the percentage of volatile thinner should be reported as the whole percentage next below the figure obtained. In the examination of samples of interior, floor, coach, and spar varnishes panel tests and drying tests on glass are made separately instead of in connection with the determination of volatile thinner, as is suggested by Brown. The distillate obtained by steam distillation of an unweighed portion of the varnish is used for the determination of the nature of the thinner.

The practically complete volatilisation of the thinner in a short time, as obtained in the determinations by Method 4, indicates that with such samples it is highly improbable that the nature of the dried film or the rate of drying is influenced by the nature of the thinner. These samples, however, were analysed shortly after preparation, while some varnishes of high quality are aged, sometimes for years, before being marketed. In aged varnishes it is probable that turpentine changes so as to yield non-volatile material, which remains in the varnish coat when the film dries. The changes in the volatile thinner contents of varnishes on ageing is under investigation in this laboratory.

VI. *Summary.*

It has been shown that any of the methods described above give results which, though only approximate from a scientific standpoint, are satisfactorily accurate for practical purposes. The volatilisation of the thinner, in some cases turpentine and in others mineral spirits, from drying films of freshly prepared varnishes, was practically complete in two hours at room temperature (30 to 35° C.).

THE QUANTITATIVE DETERMINATION OF SILICA.[*]

By VICTOR LENHER and EMIL TRUOG.

(Concluded from p. 71).

Solubility of Silica in Hydrochloric Acid and in Wash Solutions.—In order to determine what effect the concentration of the hydrochloric acid used in taking up the dehydrated silica has on the amount of silica which passes into solution and is recovered in the subsequent dehydration, the following experiments were carried out:—

One-half grm. of pure silica was fused with 2·5 grms. of sodium carbonate, treated with hydrochloric acid, evaporated, dehydrated at 110° for two hours, and then taken up with hydrochloric acid of different strengths, as indicated in Table III. After filtering and washing to a volume of about 250 cc. the silica in the filtrate was determined by evaporation, dehydration, and filtration in the usual way. The results are given in the first three columns of Table III. The main bulk of silica filtered off after the first dehydration was further treated with acid in order to determine if more silica would go into solution. The silica was transferred from the filter papers to platinum dishes. One series was treated with hydrochloric acid in exactly the same way as before and the dissolved silica determined. The other series were treated similarly with an equivalent amount of sulphuric acid. The results are given in the last two columns of Table III.

The data in Table III. indicate that digestion with concentrated hydrochloric acid or with a considerable volume of dilute acid are both to be avoided. Hydrochloric acid (sp. gr. 1·1) appears to be about the right concentration for the first moistening of dehydrated silica. The amount used and time of digestion should be the minimum.

A comparison of the data in Table III. shows that less silica goes into solution in the second treatment. The results corroborate the work of Hillebrand (*Journ. Am. Chem. Soc.*, 1902, xxiv., 368), who has shown that hydrochloric acid has a distinct solvent action on the silica. Completeness of dehydration is not the only factor that must be considered in accounting for the silica found in the filtrate after the first dehydration. Dilute sulphuric acid has about the same solvent action as dilute hydrochloric acid, while somewhat stronger sulphuric acid has a more marked action.

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[*] From the *Journal of the American Chemical Society*, xxxviii., No. 5.

Although the amount of silica dissolved in the second treatment as given in Table III. is less than that dissolved in the first treatment, yet it cannot be concluded from this that there is a definite amount of silica present after dehydration which is more soluble than the rest. In the first extraction with hydrochloric acid there was a considerable amount of sodium chloride present, which, as the following results show, has a considerable solvent action on the silica.

Solubility of Silica in Different Wash Solutions.—In order to determine what kind of a washing solution would have the least solvent action on the silica, the following experiments were made. The silica on the filter papers from the previous work was thoroughly washed with water and then washed with 300 cc. of the respective wash solutions indicated in Table IV. The filtrates were evaporated and the silica determined in each case. The silica in 300 cc. of original wash solution was also determined in each case:—

Table IV.—*Solubility of Silica in Wash Solutions. Results in grms.*

Washed solution used.	SiO_2 in 300 cc. of blank.	SiO_2 in 300 cc. after washing.	SiO_2 dissolved by wash sol.
Distilled water	0·00040	0·00106	0·00066
1 p.c. HCl ..	0·00050	0·00138	0·00088
1 p.c. NaCl ..	0·00016	0·00243	0·00227
1 p.c. NH_4Cl	0·00094	0·00586	0·00492

The data in Table IV. indicate that distilled water has the least solvent action of any of the washing solutions used. Solutions of sodium and ammonium chloride have a distinct solvent action. All things considered, a wash solution of distilled water just acidified with hydrochloric is perhaps the most desirable. The presence of a very small amount of hydrochloric acid has no marked solvent effect on the silica, but does have the advantage of helping to remove occluded bases in the silica and preventing the silica from going into a colloidal condition, in which condition it will pass through the filter paper to a considerable extent. A wash solution, consisting of 1 cc. concentrated hydrochloric acid in 100 cc. water, appears quite desirable, and this was later used with good results.

Solubility of Silica as Influenced by Extent and Nature of Dehydration.—It was thought that perhaps if the period of dehydration at 110° was increased over two hours the silica would be made more insoluble in the subsequent acid treatment. Dehydration at one-fourth atmospheric pressure was also tried. For this purpose a vacuum desiccator attached to a filter pump was placed in the drying oven. Two samples of material, a silicate rock and a clay loam soil, were fused with sodium carbonate, and the fusion was treated with hydrochloric acid. The results are given in Table V.

The results in Table V. indicate that there is no advantage in dehydrating more than two hours or in carrying out the dehydration under reduced pressure. This indicates that the failure to recover all the silica in one dehydration is not due to insufficient dehydration, but to the great opportunity afforded by the large mass of silica for its direct solution during the acid treatment. From this it may be concluded that the dehydrated mass should be taken up with as little acid as possible, and that this acid should be allowed to act only until the bases are in solution, and then filtration proceeded with immediately.

In a further experiment the period of dehydration at 110° was extended to twenty-four hours. In this case the total amount of silica recovered in all of the dehydrations was less by several mgrms. than when a two-hour period of dehydration was used. This indicates that continued dehydration for a long period at even 110° may cause the silica to become contaminated with sufficient magnesia to seriously affect the results. It seems that when magnesia thus contaminates silica it is practically impossible by subsequent evaporations with acid and dehydration to render the silica free from magnesia.

Adopted Procedure for the Determination of Silica.

After a careful study of the results thus far reported the following procedure was adopted:—

A ½ to 1 grm. sample of silicate is intimately mixed with 5 grms. of sodium carbonate and fused in a platinum crucible. In the case of a limestone, as suggested by Hillebrand (*Journ. Am. Chem. Soc.*, 1903, xxv., 1202), much less flux is required. The cold fusion is treated with 60 cc. of hydrochloric acid (sp. gr. 1·07). After all carbonates are decomposed and the lumps are broken up evaporation on steam or water bath is proceeded with until the residue begins to powder or crumble. Further evaporation should be avoided. Breaking up of lumps and crusts greatly expedites the evaporation near the end. The residue is treated with 15 cc. of hydrochloric acid (sp. gr. 1·1), covered, and heated on the water-bath for ten minutes. After diluting with 10 cc. of water filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. of hydrochloric acid (sp. gr. 1·2) to 95 cc. of water. This filtration is preferably performed with suction. The filtrate is evaporated to dryness and until the smell of acid has practically disappeared. The residue is dehydrated at 110° for two hours, taken up with 8 cc. of hydrochloric acid (sp. gr. 1·1), covered, and heated on the water-bath five to ten minutes, diluted to about 50 cc., and filtered immediately. This filtration is performed without suction, and the washing is done with cold water containing 1 cc. concentrated hydrochloric acid to 99 cc. water. (Often a little silica sticks so tenaciously to the sides of the dish that washing fails to remove it, and in such cases it is best removed with a little piece of ashless filter paper, which is subsequently burned with the main precipitate of silica). The paper and silica from the second dehydration are placed in a platinum crucible and the paper burned. The paper containing the silica from the first dehydration is then added to the crucible and the silica is ignited to constant weight. Great care should be exercised in burning the paper, as the current of air produced by a rapidly burning filter paper is sufficient to carry finely divided silica out of the crucible. Loss in this way is more serious when the amounts of silica are quite large, in which case a platinum crucible of at least 30 cc. capacity should be used. Ignition for about thirty minutes with a Mèker burner is usually sufficient to produce constant weight. If the amount of silica is low less time may be required. Breaking up of crumbs and lumps with a stiff platinum wire aids greatly in burning the last traces of carbon and reducing to constant weight. The silica is then determined by loss, volatilising in the usual way with hydrofluoric acid after the addition of a few drops of sulphuric acid. The non-volatile residue is then fused with four times its weight of sodium carbonate and after acidifying with dilute hydrochloric acid is added to the filtrate from the silica, which is examined in the usual way for the bases.

Table VI. shows the results of analyses by the method given of two silicates, one of which was a felspar, and two limestones, one of which was dolomitic. The results of a third dehydration are also given. As indicated in the table, porcelain casseroles were used in one set and platinum dishes in the other.

The data in Table VI. indicate that the method outlined gives very satisfactory results. The duplicates agreed to within 0·1 or 0·2 mgrm., which is much better than the previous results in Table V. Two evaporations conducted as stated are sufficient to recover the silica when the acid treatment is performed as outlined. The silica

Table III.—*Solubility of Dehydrated Silica in Acid Treatments Indicated. Grms. of* SiO_2 *Dissolved.*

Method of treating dehydrated silica.	First treatment with HCl.			Second treatment with	
	a.	*b.*	Av.	HCl.	H_2SO_4 (*a*)
12·5 cc. con. HCl (sp. gr. 1·2) digested 15 min. Dil. to 25 cc. and digested 15 min. Dil. to 50 cc. and filtered	0·00251	0·00251	0·00251	0·00068	0·00103
25 cc. HCl (sp. gr. 1·1) digested 30 min. Dil. to 50 cc. and filtered	0·00230	0·00212	0·00221	0·00048	0·00136
50 cc. HCl (sp. gr. 1·05) digested 30 min. and filtered	0·00410	0·00402	0·00407	0·00286	0·00279

(*a*) The H_2SO_4 was used in amounts equivalent to the HCl.

Table V.—*Solubility of Silica as Influenced by Nature and Extent of Dehydration.*

Nature and extent of dehydration.	Material.	Grms. SiO_2 recovered in successive dehydrations. First dehydr.	Second dehydr.	Third dehydr.	Fourth dehydr.	Total first two dehydr.
4 hrs. at 110°, 1/4 atm. ..	Blank	0·0008	0·0002	0·0002	0·0001	0·0010
2 hrs. at 110°	Soil	0·7878	0·0016	0·0003	0·0004	0·7894
4 hrs. at 110°	Soil	0·7887	0·0019	0·0002	0·0004	0·7906
2 hrs. at 110°, 1/4 atm. ..	Soil	0·7873	0·0014	0·0003	0·0003	0·7887
4 hrs. at 110°, 1/4 atm. ..	Soil	0·7876	0·0016	0.0002	0·0004	0·7892
2 hrs. at 110°	Silicate	0·6491	0·0014	0·0006	0·0003	0·6505
4 hrs. at 110°	Silicate	0·6511	0·0015	0·0007	0·0003	0·6526
2 hrs. at 110°, 1/4 atm. ..	Silicate	0·6506	0·0014	0·0007	0·0002	0·6520
4 hrs. at 110°, 1/4 atm. ..	Silicate	0·6490	0·0016	0·0005	0·0003	0·6506

Table VI. *Silica Determinations with Adopted Procedure.*

Grms. SiO_2 and non-volatile residue recovered in successive dehydrations.

Material.	Evaporation in	First recovery.		Second recovery.		Total first two.		Third recovery.
		SiO_2.	N. V. R.	SiO_2.	N. V. R.	SiO_2.	N. V. R.	SiO_2.
Blank	Plat.	0·0008	0·0003	0·0002	—	0·0010	—	0·0002
Silicate 8	Plat.	0·4372	0·0008	0·0030	0·0004	0·4402	0·0012	0·0003
	Porc.	0·4329	0·0003	0·0072	0·0005	0·4401	0·0008	0·0010
Silicate 20	Plat.	0·6935	0·0011	0·0033	0·0001	0·6968	0·0012	0·0003
	Porc.	0·6804	0·0004	0·0166	0·0003	0·6970	0·0007	0·0012
Limestone 12 ..	Plat.	0·0547	0·0003	0·0020	0·0004	0·0567	0·0007	0·0002
	Porc.	0·0551	0·0003	0·0017	0·0007	0·0568	0·0010	0·0001
Dolomitic limestone 13	Plat.	0·1889	0·0004	0·0022	0·0003	0·1911	0·0007	0·0001
	Porc.	0·1880	0·0015	0·0029	0·0001	0·1909	0·0016	0·0001

recovered in a third evaporation, when platinum dishes are used, ranges from 0·1 to 0·3 mgrm. These amounts are of the same order as those obtained in blank determinations or when a fourth evaporation is made, and are to be regarded as due to contamination from the glass beakers, funnels, wash water, and acid used. Hillebrand (U.S. Geol. Survey, *Bull.* 422, 94, 1910) states that from 2—4 mgrm. of silica remain in the solution after the second evaporation and filtration. The presence of such large amounts has been entirely prevented by the method outlined. The results when porcelain casseroles are used have been favourable. The results of the third evaporation indicate that in certain cases there may be contamination from the porcelain.

In other methods of procedure the non-volatile residue frequently ranges from 2 to 6 mgrms., or even much more in basic rocks. In the method outlined this has been reduced with the materials with which we worked to about 1 mgrm. on the average for both recoveries of silica. Prevention of excessive drying in the first evaporation and the use of a hot acidified wash solution has made this possible. This is a very desirable feature, as it greatly reduces the time necessary to ignite the silica to constant weight, and hence reduces errors incident to long-continued heating of platinum, and also those which may arise in the correction for impurities which have been suggested by previous workers.

Summary.

The investigation reported was undertaken for the purpose of making the determination of silica more accurate and expeditious. Certain causes of error were first investigated, and later remedies worked out and applied. The errors and corrections may be summarised as follows:—

Dehydration above 110° leads to erroneous results. Long-continued baking of a *large mass* of silica at 110° is objectionable, since the result is to greatly increase the non-volatile residue. When natural silicates are analysed, as is well known, it is impossible to recover all the silica in one dehydration, no matter how complete the dehydration may be. This is due to the fact that silica has a distinct solubility in hydrochloric acid, the extent of which is dependent on the strength and volume of acid used and time of contact. The presence of considerable impurities in the silica is objectionable, since it greatly increases the time necessary for ignition to constant weight, and may also cause an error in the correction of silica for impurities.

The difficulties just stated are overcome by the modified procedure outlined, the essential features of which are as follows:—The main mass of silica is removed after simple evaporation on the water or steam bath till the material begins to get granular but still contains considerable acid and water. In this way opportunity for the contamination of the silica is greatly lessened, as is also

the amount of non-volatile residue, which is further decreased by the use of the wash solution recommended. A dehydration temperature of more than 110° should never be used. After the second dehydration the solution of appreciable amounts of silica is prevented by limiting the amount and strength of acid used and also the period of its contact.

Our experience as well as our students' experience with this procedure as outlined has given more accurate silica results than any other procedure, and with the purpose of calling the attention of the analyst to some of the pitfalls in the determination of silica and in the subsequent determination of the bases the following observations are appended, all of which our laboratory experience has induced us to emphasise, though some have been repeatedly pointed out :—

1. In the sodium carbonate fusion method with silicates there is always a non-volatile residue when the silica is volatilised with hydrofluoric and sulphuric acids.

2. The non-volatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.

3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion the temperature should never be allowed to go above 110°.

4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used this error is almost negligible.

5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion an inherent error is obviously thus introduced.

6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminium, which do not dissolve completely in hydrochloric acid.

7. Hydrochloric acid (sp. gr. 1·1) in minimum amount should be used first to wet the dehydrated chlorides, and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off as quickly as possible.

8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then commonly hydroscopic.

9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.

10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the solutions which act as solvents.

11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.

12. Excessive time of dehydration—viz., four hours—possesses no advantages.

13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4—5 parts sodium carbonate to 1 of silicate. Less than four parts of sodium carbonate is frequently insufficient to completely decompose many silicates.

14. The non-volatile residue has been found to be invariably free from sodium. Pure silica on fusion with sodium carbonate subsequently gives no non-volatile residue.

Institute of Chemistry.—A collection of British-made laboratory apparatus will be on view at the Institute, 30, Russell Square, London, W.C., during the months of August and September, 1916, between the hours of 10 a.m. and 6 p.m. on weekdays (Saturdays 10 a.m. to 1 p.m.).

THE CARBOHYDRATES AND THE ENZYMES OF THE SOY BEAN.*

By J. P. STREET and E. M. BAILEY.†

In recent years various soy bean preparations have come into quite extensive use as special foods for the diabetic. The soy bean is especially suited for such a dietary as it is very rich in protein and fat, and, furthermore, contains only traces of starch. Notwithstanding this almost complete absence of starch, analyses of commercial flour made from the soy bean invariably show from 20 to 25 per cent of nitrogen-free extract. A number of investigators have studied this nitrogen-free extract from various points of view, but as far as the writers are aware no complete separation of the different carbohydrates existing in the soy bean has been published. The form of these carbohydrates is vital to the claims of the soy bean as a valuable food for the diabetic, for starch is by no means the only carbohydrate objectionable to those afflicted with diabetes. The purpose of the present study therefore was to attempt a rather complete quantitative separation of these carbohydrates in the material in question.

The literature of the soy bean is very voluminous, and no attempt will be made to review it here. The published analytical data are indeed conflicting. One author found 9·3 per cent sucrose, others only 3 or 4 per cent, or less. Likewise, certain European investigators report from 3 to 5 per cent starch, while Japanese chemists have not identified starch in the native soy bean. Many analyses of our own confirm the Japanese standpoint. These discrepancies as to starch content are probably due to the ripeness of the beans, or rather to the method in which they are allowed to ripen. Harz (*Zeit. Allg. Oesterr. Apoth. Ver.*, 1885, xxi.i., 40) found that when the beans do not ripen thoroughly or when they are allowed to ripen after the vines are cut, starch may be present, certain varieties being more likely to contain it than others, whereas if the beans are thoroughly ripened they are practically free from starch. Numerous authorities, including Schulze, Maxwell, and Levallois, have identified galactan in the soy bean, Levallois (*Comptes Rendus*, 1881, xciii., 281) finding 9 to 11 per cent. Likewise, Borghesani (*Staz. Sper. Agrar.*, 1907, xl., 118) found from 2·86 to 3·86 per cent pentosan in five varieties.

For the past two years various varieties of soy bean have been grown on the Experiment Station Farm. Calculated to a uniform moisture content of 10 per cent these showed compositions given in Table I.

Typical analyses of commercial soy bean flours made in the laboratory of the Connecticut Agricultural Experiment Station also appear in Table I.

A comparison of the analyses of the soy beans and the commercial soy bean flour shows that the latter contains much more protein and fat, and considerably less of all the other ingredients, doubtless due to bolting and other purifying manufacturing processes.

The beans selected for the present investigation were of the Hollybrook variety and grown on our own farm. Table II. is a summary of their analysis expressed in percentages.

The scheme of analysis, in brief, was to treat the finely ground meal successively with boiling 95 per cent alcohol, cold water, malt extract, 1 per cent hydrochloric acid, and 1·25 per cent sodium hydroxide, and to determine the kind and amount of carbohydrate removed by each of these solvents.

Alcohol Extract.

The bean meal was freed from fat with petroleum ether, and the dried residue then boiled under a reflux condenser with neutral 95 per cent alcohol for eight hours. By this treatment reducing sugars, dextrose, lævulose, invert sugar, and maltose, as well as sucrose and raffinose, are extracted. Raffinose is less soluble in alcohol than the other sugars named, according to Beilstein 1 grm. being soluble in 1000 cc. of cold 90 per cent alcohol, freely soluble in 80 per cent alcohol at 60° C., and slightly soluble in boiling absolute alcohol. The same authority states that 0·9 part of sucrose is soluble in 100 parts of 90 per cent alcohol at 14° C., and 1 part in 250 parts of cold 97 per cent alcohol. From this it is seen that while raffinose is much less soluble in alcohol than sucrose, it is somewhat soluble in boiling absolute alcohol, and therefore would be more so in boiling 95 per cent alcohol. It is estimated that in the portions digested with the boiling 95 per cent alcohol not over 1 grm. of raffinose was present in a volume of from 400 to 450 cc. of alcohol It seems reasonable therefore to assume that practically all of this sugar was removed at this stage, especially as it is known that sucrose and raffinose are, in most cases, removed together, and that, in spite of their difference in solubility, it is extremely difficult to separate them.

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† Credit for the chemical work reported in this paper is entirely due to Dr. Bailey.

TABLE I.

Variety.	Water.	Ash.	Protein N × 6·25.	Fibre.	N-free extract.	Fat.
Soy Beans Grown on Experiment Station Farm.						
Ito San	10·00	4·90	39·29	3·91	26·64	15·26
Ito San	10·00	4·76	39·96	3·85	25·67	15·76
Quebec	10·00	5·26	38·24	3·57	25·86	17·07
Quebec	10·00	5·64	40·46	3·68	24·88	15·34
Kentucky . ..	10·00	5·54	36·55	4·37	26·82	16·72
Medium yellow	10·00	4·68	40·99	3·79	25·27	15·27
Manhattan ..	10·00	7·77	40·66	3·67	23·58	14·32
Ebony	10·00	5·16	40·59	5·21	24·97	14·07
Peking	10·00	6·29	37·70	5·87	27·11	13·03
Medium green .	10·00	4·85	40·66	4·10	24·55	15·84
Okute	10·00	5·83	38·56	4·73	25·02	15·86
Wilson	10·00	5·09	37·38	5·78	27·56	14·19
Arlington . ..	10·00	5·19	35·07	5·81	29·55	14·38
Swan	10·00	6·88	39·15	4·64	26·30	13·03
Morse	10·00	4·67	37·75	4·98	28·42	14·18
Cloud	10·00	5·64	37·23	5·43	28·98	12·72
Mikado	10·00	5·33	33·15	5·03	29·59	16·90
Wing's mongol	10·00	5·98	35·59	5·46	20·97	16·00
Hollybrook ..	10·00	5·73	38·49	4·28	28·44	13·06
Average ..	10·00	5·54	38·29	4·64	26·64	14·89
Commercial Soy Bean Flours.						
	4·9	4·4	45·7	1·9	22·6	20·5
	4·2	4·2	43·1	2·2	24·9	21·4
	3·0	5·0	42·3	5·4	24·5	19·8
	4·4	4·6	42·3	4·7	25·8	18·2
	7·8	4·4	39·9	3·9	24·9	19·1
	6·5	4·1	41·0	3·4	25·0	20·0
	4·6	5·1	42·9	4·2	22·4	20·8
Average ..	5·1	4·5	42·5	3·7	24·3	19·9

The alcohol extract was evaporated nearly to dryness and then taken up with water, the solution thus obtained not being clear. One cc. of basic lead acetate was added, causing a considerable precipitate, and the excess of lead removed with anhydrous sodium sulphate. A clear straw-coloured solution resulted, in aliquots of which polarisations and reductions of Fehling's solution were made before and after inversion.

The direct reducing power of the solution was very slight, an aliquot corresponding to 20 grms. of the original material yielding only 0·0319 grm. of Cu_2O, equal to 0·07 per cent of invert sugar. After inverting 50 cc. of the solution in the usual way, an aliquot corresponding to 5 grms. of the original substance yielded 0·4367 grm. of Cu_2O, equal to 4·27 per cent of sugar, calculated as invert sugar and sucrose,

TABLE II.

Water.	Ash	Protein (N × 6·25).	Ether extract.	N-free extract and fibre.	Total.
12·67	4·64	36·69	14·92	31·08	100·00

Constituents included in Nitrogen-free Extract.

Galactan (*a*)	4·86
Pentosan	4·94
Organic acids (as citric)	1·44
Invert sugar	0·07
Sucrose	3·31
Raffinose	1·13
Starch	0·50
Cellulose	3·29
Undetermined hemicelluloses	0·04
Dextrin	3·14
Waxes, colour principles, tannins, &c. (by diff.) ..	8·60
Total	31·32
Galactan from raffinose	0·24
Per cent N-free extract and fibre	31·08

(*a*) Including 0·24 per cent galactan from raffinose.

The direct polarisation of the solution, calculated to the basis of normal weight of original material in 100 cc., and read in a 200 mm. tube, was + 5·4° V. at 14—15° C. The invert readings for the same amount of material were practically zero, the average of ten readings being +0·02° V. Polarisations of a duplicate alcohol extract prepared as above gave a direct reading of + 5·3° V., and an invert reading of +0·06° V.

The fact that the invert readings were not decidedly minus indicates the presence of some sugar other than sucrose. A sucrose solution reading +5·4° V. direct, on hydrolysis should read − 2·3°. There is present, therefore, some simple sugar, or a complex one which hydrolyses into dextro-rotatory sugars, which counterbalance the lævulose rotation. This sugar cannot be dextrose or maltose because of the slight direct reducing power of the solution. Three qualitative tests were made which bear on the identity of the sugar or sugars in the alcoholic extract.

Osazone Formation.—The simple hexose sugars in a state of purity form osazones in less than twenty minutes. Sucrose forms glucosazones in about thirty minutes, but, as Browne and others have noted, the presence of organic matter, such as other sugars, greatly affects the rate of the osazone formation. After heating the direct solution about one and three-quarter hours a considerable amount of glucosazone was formed, m.p. 201—203° C., rapid heating (this should be 204—205°). According to Tollens, raffinose yields an osazone after about two hours, its m.p. being 187—189° C. The osazone observed by us is apparently due to sucrose, its formation being retarded for the reason noted above.

Invertin Test.—The enzyme invertin hydrolyses sucrose into reducing sugars; it also acts upon raffinose, and its failure to produce reducing sugars at all in the direct solution would indicate the absence of either of these sugars. It was found, however, that 0·1 grm. of invertin acting upon 2 cc. of the direct solution for fifteen minutes at 60—65° C. caused a heavy precipitate of Cu_2O with Fehling's solution.

Emulsin Test.—Emulsin hydrolyses raffinose but is without action on sucrose (Neuberg, *Biochem. Zeit.*, iii., 519):—0·1 grm. of emulsin + 10 cc. of direct solution + 10 cc. of water, incubated at 38—40° C., for about two hours, gave a very decided increase in reduction over a blank in which the action of the enzyme was inhibited by boiling.

From the above data, therefore, it is concluded that raffinose is present, and that we are justified in using

Creydt's formula for sucrose in the presence of raffinose, in estimating these sugars from the polarimetric readings :—

$$\text{Sucrose} = \frac{0{\cdot}5188\,a - b}{0{\cdot}8452} = 3{\cdot}31 \text{ per cent},$$

$$\text{Raffinose} = \frac{a - \text{sucrose}}{1{\cdot}852} = 1{\cdot}13 \text{ per cent},$$

or a total of 4·44 per cent as against 4·27 per cent obtained by copper reduction as noted above.

Cold Water Extract.

The alcohol-extracted material was dried and weighed; 13·024 grms. of this residue were digested with 200 cc. of cold water for twenty-four hours, filtered, and the water-insoluble material washed with about 200 cc. of cold water. The water extract was partially evaporated at 60—70° C., a little sodium carbonate being added to neutralise the faint acidity, and made up to a volume of 200 cc. The solution was opalescent, and required the usual treatment with basic lead acetate before polarisation.

The direct reducing power of the solution was very slight, an aliquot representing 1·628 grms. giving no visible copper reduction. After hydrolysis for two and one-half hours with the usual amount of hydrochloric acid (sp. gr. 1·125), an aliquot representing 0·814 grm. gave 0·1710 grm. of Cu_2O, the precipitate being of a yellowish red colour. This is equivalent to 5·73 per cent calculated as dextrin in the original material. It will be shown later that much of this reduction was due to pentosan and galactan.

Direct polarisation on the basis of normal weight in 100 cc., in a 200 mm. tube, showed $+11{\cdot}5°$ V. at 10° C.; after the usual inversion for ten minutes the reading was $+5{\cdot}7°$ V., and after hydrolysis for two and one-half hours it was $+4{\cdot}4°$, both readings at 10° C.

The solution though opalescent gave a negative test for soluble starch. After adding strong alcohol to an aliquot of the water extract and allowing to stand for several days, the white gelatinous precipitate was filtered off, the filtrate evaporated, and the latter after making up with water to the same basis as above polarised $+1{\cdot}4°$ V., showing that the strong rotatory power was due to substances precipitable by alcohol, such as dextrin, vegetable gums, and mucilages.

A test for mucic acid in the direct solution gave at first negative results, but after standing considerably longer than the prescribed time a white crystalline residue was obtained of the general appearance of mucic acid (m. p. 214° C., r.h.). This indicates the presence in the water extract of a galactose-yielding sugar, or complex, besides dextrin, and might be due to a small amount of raffinose not entirely removed by the boiling alcohol, but more probably to water-soluble galactan in the form of, or derived from, the vegetable gums and mucilages referred to above. (The very close agreement in the polariscopic readings of the two extracts prepared with 95 per cent alcohol, the second one being digested twice as long as the first, however, makes it improbable that any raffinose could have been left in the residue from the alcohol extraction).

Malt Extract Digestion.

Four grms. of the material extracted with ether and boiling alcohol were washed with cold water, first by decantation and then on the filter, until the washings amounted to about 300 cc., and failed to reduce Fehling's solution on treatment with hydrochloric acid. This residue was digested with freshly prepared malt extract in the usual manner for two ninety-minute periods. The solution was then hydrolysed and its reducing power determined, showing the equivalence of 0·50 per cent of starch in the original material.

(To be continued).

A PLEA FOR A CHEMISTS' PROTECTIVE ASSOCIATION.*

By ROLLIN G. MYERS.

For several years the writer has been studying the conditions under which many of the technical chemists work in the laboratories of this country. More than once he has planned to place his ideas before the American Chemical Society, but other more pressing matters intervened. Now the time is ripe. In the first place it is to be clearly understood that these observations are not second-hand nor the conclusions altogether *a priori* in character. For nearly ten years the writer was connected with different companies—twice as chief chemist, several times as first and second assistants in iron, steel, cement, and water laboratories. Besides this he made reports of several technical researches connected with the chemistry of the carbon incandescent lamp. For nearly a year he was assistant in the U.S. Referee Laboratory of Prof. John H. Long, North-Western University of Chicago, while at the present time and for the past five years he has been a teacher in chemistry. He has had more than a passing interest in the welfare of the chemist in practical life, more specifically the technical chemist. In view of the writer's experience he asseverates that his arguments deserve serious attention and the practical part of his thesis a trial.

Lack of Practical Organisation among Chemists.

To the most observing and thoughtful members of the profession one thing clearly presents itself—the lack of practical organisation among chemists. The American Chemical Society and the various alumni associations of the technical schools and universities are organisations, it is true, but their aims are scientific and social rather than practical. The Chemists' Club of New York represents a movement towards practical organisation, but its scope is not broad enough to satisfy some of the more fundamental and pressing wants, only vaguely expressed at times by the technical members of the profession. For several years this idea of practical organisation has been a recurrent one in the mind of the writer. But for what ends? The first, to increase the financial return of chemists; the second, to raise chemistry to its rightful and just place among the professions. The first end is the more important and cogent. For this reason the writer will make it play a predominant part in the discussion to follow.

What is a Chemist?

In view of the ridiculously small wage chemists receive any attempt to remedy this condition is worth while. Moreover, the practical bearing which this element of social life has on the struggle for existence is of profound significance. Every chemist quickly realises this. Before dealing with the wage problem and its solution several questions closely related to it must be discussed. One of these is connected with the common application of the word chemist. There is a manifest dilatoriness on the part of many of the profession, and naturally the public at large, in the use of this word. It is applied indiscriminately to trained and untrained persons. In certain parts of Pennsylvania, for example, a boy who has served for a few days in an iron laboratory, frequently not even a high-school graduate, is called a chemist. In many other parts of the country the same custom prevails. Frequently there is a confusion of chemist with druggist. There are people who even look at the chemist as a follower of the "black art," to be respected but to be somewhat feared. In fact the chemist may be anything or nothing, and he is frequently less respected than a plumber or a mechanic. It is therefore imperative to define the word chemist and restrict it to the class which it defines. What, then, is the definition of chemist? Chemist is applied to that class of persons who have spent four or more years at an accredited technical school or university in the didactic and laboratory study of all the regular branches of chemistry, and who have received formal statements represented by a degree or degrees, that the prescribed courses of study have been satisfactorily completed. A chemist, therefore, is a trained man; he belongs to a profession which in practical usefulness is unexcelled.

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* Presented before the Louisiana Section of the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 9.

But why do these persons spend four or more years preparing for a profession? First, for a life work; second, for the truly practical object of making a living. They are thoroughly serious in this matter; it is not the result of a passing fancy nor always a pleasing thought; neither is it for some temporary situation, until something else appears in another line of work which promises greater emolument. These persons train themselves for a purpose and pursue this purpose to the end.

In addition, it cannot be denied that the standing of the chemist is equal to that of the other professions. This is true, since the requirements for admission, as well as the intellectual ability required to complete a chemical course, are as high, often higher, than those demanded for courses in law, medicine, dentistry, or pharmacy.

Neither can it be denied that the chemist should have a financial return for his services proportionate to his training, not only by reason of the cost of his training but on account of his professional standing as well. Since this question of emolument is cardinal to the whole discussion it is absolutely necessary to decide upon how much the chemist should receive. As a provisional arrangement the writer submits the following estimate of salaries. Assistant chemists who enter laboratories should receive not less than 1200 dols., with a yearly increase of 200 dols. to a limit of 1800 dols. per annum. Chief chemists should receive not less than 2000 dols. and be limited to 5000 dols. per annum.

Reserving this question of salaries for later discussion and confining the attention to the arguments so far advanced, two principal conclusions and one subordinate conclusion have been arrived at:—

1. That the profession of chemistry should be limited to those who have spent a definite period of time in training themselves in a technical school or university for work in practical and research laboratories.

2. That chemists should receive just salaries proportionate to their standing and the high quality of their work.

3. That a just though tentative scale of salaries should be within the limits of 1200 to 1800 dols. per annum for assistants and 2000 to 5000 dols. per annum for chief chemists.

These conclusions place all subsequent discussion on firm and definite ground. In addition they suggest formulated ideals for the chemist to strive for, though it cannot be too greatly emphasised that their realisation can come about only by organisation. While that conclusion relating to salaries has been given precedence and should be the principal end of any practical organisation, the other conclusion relating to the personnel of the chemical profession has an intimate bearing on the attainment of this end and should be always in mind. However, in order to form correct judgments, which have a determining influence on the choice of methods in the attainment of an end, these judgments must not only include the ideal aims but a knowledge of the actual conditions under which the chemist works. What, then, are the actual conditions which are common in practical laboratories? To be more specific and clear this question can better be resolved into two: (1) What is the actual rank and file of the workers in the practical laboratories of this country? (2) What are the actual salaries which these workers receive?

Taking these questions in order, it requires but little observation and less practical experience to learn that a large number of these workers are not chemists. They can be divided roughly into two classes—quasi chemists and laboratory boys. The quasi chemists may be placed in three divisions: (*a*) persons who have academic degrees from universities, but who have not specially qualified themselves for chemical work; (*b*) persons who have had from one to three years' chemical training in an accredited technical school or university; (*c*) persons who have graduated from or who have taken chemical courses in the correspondence schools, and whose training is little better than none at all. The laboratory boys include persons, frequently of immature age, who have had no chemical training and whose knowledge is confined to a few technical methods and some chemical principles vicariously obtained from text-books and from the chemist himself. Many of this latter class have charge of laboratories, and this is an unfortunate fact.

Compared to the personnel of the professions of medicine, dentistry, pharmacy, and law that of the chemical profession is low indeed. Medicine is the only profession which furnishes an approximate parallel, but even here the untrained members are the exception and not the rule. Many of the trade unions have a higher personnel than the chemical profession.

Present Salaries of Chemists.

The answer to the second question—*i.e.*, the actual salaries received by the chemical workers—is given on the basis of the writer's personal experience and observation. It represents a mean of the salaries paid to the subordinates and to those in charge of laboratories. The writer is positive that his estimates are correct ones. The assistants in laboratories receive 65 to 75 dols. a month, or 780 to 900 dols. per annum. Those in charge of laboratories receive 90 to 200 dols. a month, or 1080 to 2400 dols. per annum.

So far the writer has confined his discussions to arguments which emphasise the need of a practical organisation among chemists. These arguments have been strengthened by contrasting the ideals of the chemist with the actual conditions met with in chemical laboratories. That the actual conditions are far from ideal is evident in the painfully low personnel and the miserable wage. Before proceeding to the final discussion in respect to the adoption of ways and means for remedying these evils it is but proper to make a critical study of the interrelationship of these conditions as well as the causes which are directly or indirectly instrumental in producing them.

Relation between Personnel and Wage.

One can hardly question the close relation which exists between personnel and wage; in fact it may be contended that either one may become the function of the other. If there is a low personnel there is a low wage. This harmonises with the general observation that the employer really prefers a trained to an untrained person, and consequently may be persuaded to pay more. It is also true that a low wage may produce a low personnel, for a trained man objects to working for nothing, and naturally selects a laboratory, if he can find one, where the emolument is greater. But the mere fact that this relationship exists between these prevailing conditions is not satisfying, for there appear to be deeper and more fundamental causes of these effects at work. One of these causes, which to the writer's mind is extremely potent, is the one-sided standard of wages determined for the chemist by business men. This is unfair and unjust—unfair in that the employer takes advantage of the inability of the chemist to raise objections of material aid to himself, and unjust in that the chemist is not given a voice in the settling of a wage which has such vital meaning to his existence. The judgment of the business man is usually mercenary in character. With him the problem consists essentially in getting as large a financial return as possible for the money invested. What is more, in most cases he solves the problem successfully. It is easy enough to conclude that a certain employee is worth only so much. The reason that he is worth only so much is because the business man needs to pay him only so much. Besides, it is a very satisfactory thing from the business man's side, for it means that his profits are just that much more. How much more satisfactory it would be if the employee could be induced to work for nothing!

(To be continued).

THE BOARD OF SCIENTIFIC SOCIETIES.

On the initiative of the Royal Society a Board of Scientific Societies has now been established for the furtherance of the following objects:—

> Promoting the co-operation of those interested in pure or applied science; supplying a means by which the scientific opinion of the country may on matters relating to science, industry, and education find effective expression; taking such action as may be necessary to promote the application of science to our industries and to the service of the nation, and discussing scientific questions in which international co-operation seems advisable.

The Board at present consists of representatives of twenty-seven scientific, including technical, societies. The regulations give power to add to this number and to appoint as members of sub-committees individuals who are not necessarily connected with any of the constituent societies.

An Executive Committee has been appointed consisting of the following members:—Sir Joseph Thomson, O.M., P.R.S. (Chairman); Dr. Dugald Clerk, F.R.S.; Sir Robert Hadfield, F.R.S.; Mr. A. D. Hall, F.R.S.; Prof. Herbert Jackson (Hon. Secretary); Sir Alfred Keogh, K.C.B.; Sir Ray Lankester, K.C.B., F.R.S.; Prof. A. Schuster, Sec. R.S.; Sir John Snell; Prof. E. H. Starling, F.R.S.; Lord Sydenham, G.C.S.I., F.R.S.; and Mr. R. Threlfall, F.R.S.

The first meeting of the Board was held on July 20, when important questions relating to scientific, educational, and industrial matters were under consideration, with a view to taking effective steps for co-ordinating the work carried out at present by a number of independent bodies, or initiating action in the case of other matters of national importance.

NOTICES OF BOOKS.

Coal-tar and Ammonia. By George Lunge, Ph.D. Fifth Edition, greatly enlarged. London: Gurney and Jackson. 1916. In Three Parts, not sold separately. Pp. 1718, 8vo. Price £3 3s. net.

Although only a comparatively short time has elapsed since the fourth edition of this work was issued there will be no doubt but that the fifth edition will be welcomed as cordially as its predecessors. In preparing it the most recent text has been particularly thoroughly and carefully revised, and, moreover, a very large amount of new matter has been added. It is only necessary to look through the pages which contain references to and brief extracts of publications made during the printing of the fifth edition to realise how very rapidly the literature of the subject is growing and new processes are being suggested and investigated, and it is not surprising that this new edition has grown to the dimensions it has now reached, which are about one and a-half times that of the latest. The first part deals fully with coal-tar itself, its preparation, properties, and uses. In Volume II. pitch, creosote, carbolic oil, and other derivatives are treated, while Volume III. is devoted to ammonia. It is this part in particular which has been greatly enlarged, many new processes for the preparation of ammonia and its salts having been recently worked out. No other work on coal-tar and ammonia is in any way comparable with Dr. Lunge's standard treatise which with the utmost comprehensiveness deals with every aspect of the subject. The arrangement is so excellent that in spite of the enormous amount of material any detail can be looked up in the shortest possible time, and the indexing has been very efficiently performed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 22, May 29, 1916.

This number contains no chemical matter.

No. 23, June 5, 1916.

Devitrification of Crystal Glass.—H. Le Chatelier.—Devitrification has hitherto been observed only in the case of glasses containing lime. Monocalcic silicate is then formed, $CaO.SiO_2$, and appears in one of its two dimorphic varieties; *i.e.*, hexagonal lamellæ of pseudo-wollastonite, or fine needles of ordinary wollastonite. The author has observed a case of devitrification of a lead glass from which crystals of silica were obtained, in the form of one of its varieties of low density, tridymite. This is the first example of the crystallisation of silica in the devitrification of glass.

Formation of Pyridic Bases by Condensation of Ketones and Amides.—Amé Pictet and Pierre Stehelin.—When acetone is dehydrated by means of sulphuric acid it is converted into mesitylene. Given the great analogy between the benzene and pyridine nuclei, it seemed probable that pyridic bases would be obtained similarly if one of the three molecules of ketone was replaced by a molecule of amide. It was found, however, that the condensation could not be effected by means of dehydrating agents (H_2SO_4, P_2O_5, $ZnCl_2$), for they simply transformed the amide into nitrile. If, however, the mixture of acetamide and acetone was heated to 250° in sealed tubes a very small yield (about 2 to 3 per cent) of symmetrical trimethylpyridine was obtained. Similarly one molecule of benzamide and two of acetophenone heated to 275° gave symmetrical triphenylpyridine. Attempts to synthesise pyridine itself by substituting aldehydes for ketones in this reaction were a failure, although a small quantity of α-picoline could be obtained from a mixture of paraldehyde and acetamide.

MISCELLANEOUS.

Balances.—In issuing a new catalogue for 1916 Mr. L. Oertling, the well-known balance maker, states that the instruments are all manufactured in London, which is and always has been the address of the firm since its establishment in 1849. The list includes all forms of balances, from the student's simple balance to the latest short beam aluminium alloy Instrument, together with special sets of weights, suitable for all purposes; also hydrometers, saccharometers, &c. Mr. Oertling's balances are so well known that further notice is unnecessary, but it speaks well for the vitality of this old-established London house that it has been able to prepare a new and well-illustrated list at a time when the difficulties of publication are considerable.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Colouring Matters for Confectionery.—A correspondent wishes to know the names of firms who supply colouring matters for high-class confectionery.

THE CHEMICAL NEWS.

Vol. CXIV., No. 2961.

THE REVIVAL OF THE USE OF NATURAL DYESTUFFS.*

By EDWARD S. CHAPIN.

Imagine if you can the following situation:—The supplies of artificial dyestuffs have become exhausted; the European blockade or embargo, call it what you will, has continued in uninterrupted force; capital has been too timid to manufacture artificial dyestuffs in this country. This situation we will now consider. "Nothing but black and white," says one; "The country will have to wear white," cries another; a third asserts, "The mills of the country will have to shut down!" What is the truth? The truth is that natural dyestuffs can keep the mills of the nation in operation, producing a diversification of shades and giving fast colours.

This paper does not propose to consider the question of the relative merits of natural dyestuffs *versus* artificial dyestuffs. The present is no time for controversy; it demands co-operation and construction. We must remember that before the days of the modern artificial dyes people wore coloured garments. Ladies were gay and gallants tried to please long before Perkin discovered mauve. A careful reading of any of the works of the masters of detailed description of the past century—of Dickens, Thackeray, Victor Hugo, or Goethe—will reveal interesting evidence of colour and coloured fabrics. Even more so the standard text-books on dyeing of fifty or seventy-five years ago consider the whole range of the spectrum. It is truly remarkable the multicoloured and fast effects that the dyers of the old school achieved with limited means and facilities. It is quite within the memory of many of this audience, when the earlier aniline colours were distrusted by the general public because of their comparative fugitiveness, and it took much industrious advertising and scientific development of new and better products to overcome this prejudice.

The dyers and chemists of to-day are in a position to secure with natural dyestuffs better results than the dyers of former days. The forms of natural dyestuffs were not so perfect formerly as to-day. Then the dyer was forced to use the dyestuffs in the form of chips or ground bark or ground leaves; to-day he has ready at hand the essential colouring matter of the natural dyestuffs in the form of extracts, pastes, or powders, and in many instances the colouring matters have been worked up by chemical treatment so that they dye more readily and give brighter and faster results. The march of chemical and mechanical science contributes to the solution of the task. Chemical science in recent years has found the exact chemical composition and nature of the natural dyestuffs, so that they can now be dyed most intelligently and in accordance with the highest development of the theory and the practice of dyeing. New and improved chemicals and dyeing assistants are at the disposal of the dyer; new forms of dyeing apparatus and improved mechanical devices help further. Improved dyeings are to be expected in response to persistent and intelligent work, and during the past months such results have been secured in many instances.

Available Natural Dyestuffs.

For the dyeing of cotton the following natural dyestuffs are available: logwood, fustic, bark or quercitron, flavine, hypernic and the various redwoods, catechu or cutch, gambier, sumac, madder, Persian berries, and indigo. Of these dyestuffs all except madder, Persian berries, and indigo are available in large quantities.

Logwood is the product of a large tree known botanically as *Hematoxylon campechianum*, which grows abundantly in the West Indies and Mexico. The supply of logwood is not petering out, as some have erroneously imagined; the logwood forests have not all been cut off. There are well-nigh limitless virgin forests of logwood in Haiti, Jamaica, and Mexico. Reafforestation and cultivation are the simplest of operations. The logwood tree is a veritable weed—it spreads itself; twelve years alone elapse between the seed and the tree ready for cutting for commercial purposes. Cultivation consists in keeping the forests thinned out, so that the luxuriant tropical growth will not form an impenetrable jungle. It may fairly be said that never before has there been available more logwood than to-day.

Fustic, also known as old fustic, Cuba wood, and yellow wood, comes from a tree known botanically as *Morus tinctoria*, or *Maclura tinctoria*. It is a native of Brazil, Mexico, and several of the West Indian islands. Quercitron bark is the inner bark of a species of oak, the *Quercus nigra*, or *Quercus tinctoria*, a native of America. It grows abundantly in Pennsylvania, Georgia, and the Carolinas. Flavine is the name given to a preparation of quercitron bark. It contains the principal colouring matter of quercitron bark, quercetin, in nearly chemically pure state. Hypernic is the name given to the colour extracted from the various soluble redwoods. These are principally Brazil wood, peach wood, sapan wood, and lima wood. Brazil wood grows in the forests of Brazil, peach wood is a native of Mexico; sapan wood grows in Siam, Japan, and the East Indies; lima wood is imported from Peru. Catechu (or cutch) and gambier closely resemble each other in properties; they are obtained from various species of acacia, areca, and uncaria, growing in India. Sumac consists of the leaves, leaf-stalks, and small twigs of several species of *Rhus*; this shrub is remarkably common and widely spread, growing in Sicily, Tuscany, France, Spain, Algeria, Canada, and the United States, particularly in Virginia.

The various regions from which these natural dyewoods come are, with unimportant exceptions, outside the inhibiting influence of the war; accordingly they are all available. Even prior to the war these dyestuffs were in large general use, much more extensively than is generally realised, so that the present additional demands from the textile mills find an industry well fitted to take on extra burdens and to perform needed services.

Black Dyeing of Cotton

Black is the colour most widely demanded by the trade, and will accordingly first engage our attention. For black dyeing logwood has been and still is the most generally all-round useful black dyestuff. It can be used not only for the colouring of cotton but also of wool and silk and a great variety of fibres. There are three methods of applying logwood on cotton—(1) the stuffing and saddening, (2) the bluestone soda-ash, (3) the mordanting methods.

The Stuffing and Saddening Method.

In this method of dyeing, the cotton, as piece goods, yarn, or raw stock, is first impregnated with the logwood by passing it through or boiling it in a concentrated logwood extract solution; it is then dried or whizzed to fix the logwood or remove an excess not taken up by the fibre; finally it is passed through a bath of chemicals, usually chrome, or chrome and bluestone, or copperas, to develop the black. Two illustrations of this process will be given—one on piece goods and the other on raw stock.

Logwood Black on Piece Goods.—This process makes use of two boxes, and has been in constant successful use for the past four years in the dyehouse of a large producer of black dyed cotton piece goods.

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* Address before the Ninety-eighth Meeting of the National Association of Cotton Manufacturers, Boston, April 28 and 29, 1915. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 7.

The apparatus consists of a stock tank for the logwood liquor and a logwood dye-bath, three sets of drying cans, a stock tank for the chrome liquor and a chrome bath, a steam box, a wash mangle, and a washer. The logwood box and the chrome box are provided with guide rolls, and above the centre of each box are three squeeze rolls. The guide rolls and the squeeze rolls are so related that the cloth in its passage through both the logwood and the chrome bath is twice immersed and twice squeezed.

The dry bleached pieces are run into the dye-bath and over the first four rolls, squeezed, and given a second run in the dye-bath over the second four rolls, followed by another squeeze. From the dye-bath the pieces are dried over three sets of drying cans. The passage through the chrome bath follows immediately, and here, as in the dyeing, there are two immersions and two squeezes. After the chroming the goods are steamed and then washed. The washing is very thorough, first by passage through a wash mangle and then through a washing machine. After washing, the goods are again dried and then finished.

Stock Liquor.

125 gallons water.
110 lbs. logwood extract, 51° Tw.; 5 gallons acetic acid, No. 8.
Temperature of dye-bath, near boil.
Time of immersion, ten seconds.

Chrome Liquor.

125 gallons water.
49 lbs. bichromate soda.
3 lbs. soda-ash, 58°.
Time of immersion, about two seconds.
Time of steaming, about ten seconds.

The speed of the machine, 45 to 50 yards a minute, corresponds to a production of about 3000 yards an hour, but a speed of 75 yards to the minute (4500 yards an hour) is possible.

The goods are used as linings for suitings, overcoats, and the like, where a black is needed that will not stain white when wet hot-pressed. The logwood process is preferred because of the low cost of production and the excellent fastness of the result.

Logwood Black on Raw Stock.—The following method is being employed in a Klauder-Weldon dyeing machine, colouring 1000 lbs. of cotton to a batch.

Run for one hour at a boil in a 10 per cent solution of logwood extract, prepared by dissolving 10 lbs. logwood extract, 51° Tw., to every 12 gallons of water. This solution will stand 4° Tw. at 70°. Take out of machine and whizz. Repack in machine and strike with 4·5 per cent bluestone and 1·5 per cent soda chrome. Run in striking-bath one and a-quarter hours; wash well. Soap in a 0·5 per cent solution of soap; wash and dry. The logwood-bath is saved and brought up to 4° Tw. for further dyeings. This method gives a remarkably full and rich black on stock, of excellent fastness to fulling and of moderate fastness to light.

The Bluestone Soda-ash Method.

The bluestone soda ash method of dyeing-cotton, or the ash black, as it is commonly called, is a favourite method because of its simplicity.

The following recipe is a slight modification of a bluestone soda-ash logwood black formula used in a large mill for the colouring of raw cotton, and illustrates well the general principles and practice that are obtained in the successful dyeing of cotton with logwood in the single bath:—

Dye-baths for 100 lbs. raw cotton.	Starting bath. Lbs.	Second bath. Lbs.	Third, or standing bath. Lbs.
Logwood extract, 51° ..	60	40	20
Soda-ash, 58°..	6	4	3
Bluestone	3	2	1·5

Boil one and a-half hours. Throw out the stock and allow to drain. Oxidise for two hours, or until the full shade is developed, turning occasionally.

After the standing bath is obtained enter the first lot for a second dip in the standing bath. After this one immersion is usually sufficient. If extra heavy shades of black are required give two immersions, or increase the amount of dyestuff and chemicals in the standing bath. If a deep jet shade of black is desired use an ounce of cutch extract for every lb. of logwood extract. Some dyers find it advantageous to use, also, an ounce of sumac extract for every pound of logwood extract.

The bluestone soda-ash logwood black can be utilised for the dyeing of other forms of cotton, as cotton yarn, cotton warps, and the like, and for the dyeing of a wide variety of cotton fabrics. The following series of formulæ are taken from practice:—

Dyeing Cotton Yarn.—For dyeing cotton yarn black dye is usually preferred. Black dye is a logwood extract which contains a proportion of tanning-bearing material, such as chestnut extract. It gives a very good deep black at an exceedingly low cost.

Dye-baths for 100 lbs. cotton yarn.	Starting bath. Lbs.	Second bath. Lbs.	Third, or standing bath. Lbs.
Black dye	50	25	20
Soda-ash	20	8	3
Blue vitriol	10	4	1·5

Boil one and a-half to two hours, lift and oxidise two or three hours. By after-treating with 1 per cent chrome at 150 to 160° for twenty minutes the fastness to washing is made excellent.

Dyeing Cotton Warps.—For 650 lbs. warp prepare a bath containing 130 lbs. logwood extract, 51°; 18 lbs. soda-ash; 12 lbs. blue vitriol.

Give four runs, boiling. Sadden in another tub with 6 lbs. copperas, at 120° F.; finish. This gives a very good black.

The following recipe is an example of a successful application of the use of salt in the bluestone soda-ash logwood black. A Klauder-Weldon machine was used in dyeing:—

For 800 lbs. raw cotton prepare a starting bath containing 370 lbs. logwood extract, 51°; 18 lbs. blue vitriol; 18 lbs. soda-ash; 10 lbs. common salt.

Boil the cotton for two hours; oxidise for two hours. Afterwards wash in 8 lbs. soap, 5 lbs. common salt, 15 lbs. sal soda, 1 qt. ammonia. Dissolve the chemicals for the washing in about three-quarters of a barrel of water, and feed on to the cotton at 120°. Continue washing one-half hour.

For a standing bath gradually reduce the amount of dyestuff and chemicals above given during four or five baths to one-half the quantities.

The bluestone soda-ash logwood black can be used for all purposes where fastness to fulling is not required. It is faster to light than the stuffing and saddening black.

The Mordant Methods.

By mordant methods is meant those methods in which the mordant is fixed on the cotton previous to the logwood treatment. Two of these methods will engage attention: (1) the iron, (2) the chrome.

1. *The Iron Mordant Black.*—The iron mordant logwood black has always been employed when a black of special fastness to fulling and light is required. The following recipe is for colouring warps in a four-box machine:—

Logwood Black on Warps.—Boil up 25 per cent extract of sumac in the boxes, run in the yarn, and leave over one day (thirty-six hours or more). Treat to two runs in clear lime-water, followed by two runs in pyrolignite of iron, 3° Tw.

In practice the volume of liquor in the iron liquor machine is so small that the readings of the hydrometer are not of much value. It is best to add between 20 and

25 per cent iron liquor, one-half before each run, and to squeeze the warps lightly. Much of the liquid is removed from the bath, and it is generally necessary to add some water on every set. Wait twenty to thirty minutes before washing, then treat to one run in clear lime-water and wash again.

15 per cent concentrated extract logwood, 3 per cent concentrated extract fustic, 1 per cent copper sulphate. Add one-half the logwood and one-half the fustic, bring the temperature of the bath to 140° F., and make one run. Add the remainder of the logwood and fustic, raise the temperature to 170° F., and make one run. Raise the temperature to a boil and make six runs. Add the copper sulphate in solution, half on the fifth and half on the sixth run, there being eight runs in all. Then wash with one run.

One per cent potassium bichromate. Add one-half the bichromate to make one run at 180° F. Add the remainder, and make one run at the same temperature. Wash with two runs. Finish with 3 per cent lard oil and 3 per cent soft soap (one run).

The above process can be shortened considerably with equally satisfactory results by the use of the machinery constructed for the dyeing of sulphur colours. These machines give longer immersions than the old Scotch tubs and have heavier nips.

Four-box Machine.

First run—

First box: 50 per cent sumac extract, 180° F.; nip.
Second box: 30 per cent nitrate of iron; cold; nip.
Third box: Lime solution; cold; nip.
Fourth box: Water.

Second run—

Three boxes of logwood, 30 to 40 per cent to each box, boiling.
Fourth box: Wash.

Practically the same processes may be used for pieces.

2. *The Chrome Mordant Black.*—The chrome mordant black came into being in response to the request to dye logwood blacks on raw stock in a vacuum dyeing machine. In this machine the methods above described, except the iron mordant method, do not give any results at all.

The use of a chrome mordant to develop and to fix logwood on wool is a well-known dyeing process. It yields blacks of excellent fastness to fulling, light, and various other agencies, and of exceptional beauty. The idea to adapt this method of dyeing wool to obtain equally fast and handsome results on cotton has long been alluring. Various methods of mordanting the cotton with chrome that have been tried in the past have not met with wide or permanent success.

The trouble has always been either that the chrome would not go on the cotton fibre or was deposited so loosely that in washing it nearly all came off.

These difficulties have recently been overcome by the use with the chrome of a compound (invented by a well-known chemist) which causes the chrome to exhaust on to the cotton and to be deposited so firmly that even severe washing will not strip it off.

The preliminary studies for the practical use of this new method of mordanting cotton were made in the model laboratory of the American Dyewood Company. This laboratory is fully equipped with small size dyeing machines of latest invention. Through the courtesy of Mr. W. A. Mitchell the work has passed beyond the laboratory stage. Mr. Mitchell generously offered the use of the dyehouse of the Massachusetts Cotton Mills for trials on a practical scale, and the results obtained in the laboratory of the American Dyewood Company have thus had the benefit and the test of the splendid personnel and equipment of Mr. Mitchell's plant.

The following recipe was employed in the colouring of 150 lbs. of raw cotton in a vacuum dyeing machine:—

Black on Raw Cotton.—After loading the machine fill with water and bring to a boil. Boil ten minutes to ensure thorough wetting out of the cotton. Add 6 lbs. of soda chrome dissolved in three pails of water, and after the chrome liquor has well circulated add slowly 3 lbs. of chrome assistant dissolved in two pails of cold water. Boil one hour; wash. Fill the machine with water and bring to a boil. Prepare a half-barrel of logwood extract liquor 15° Tw., containing 10 per cent fustic and six pails of clear lime-water. Boil the logwood liquor well. Add slowly to the machine and boil one hour: wash. Strike cold with 1 lb. of bluestone and 8 ozs. of chrome; wash and finish as usual. Soaping improves the beauty of the shade but is not essential.

The more concentrated the chrome liquor the more quickly the cotton takes up the chrome and the less the time required for boiling. From two-thirds to five-sixths of the chrome is exhausted on the fibre. The logwood liquor is not exhausted, but should be run off and kept for use in subsequent baths. The heavier the black required the more concentrated should be the logwood liquor.

This process gives a black of excellent fastness to fulling and to light. The stock cords readily and the feel is especially satisfactory.

The process has been tried practically only on raw cotton. It has given good results in the laboratory on yarn and pieces. As the colouring of raw cotton in a vacuum dyeing machine is the hardest test of a process there is good reason to believe that the new chrome mordant method can be adapted in practice to the colouring of the other forms of cotton and in the various other dyeing apparatus.

3. *Fashion Shades on Cotton.*—Next in importance to black come the fashion shades. Many artificial colours are so brilliant that the great fear of many people has been that without these the consuming public could not be satisfied. A few illustrations will show that besides blacks the natural dyewoods can be made to yield a wide variety of fashion shades.

In dyeing the fashion shades the stuffing and saddening method and the mordant method are applicable.

Catechu (or Cutch) and Gambier Browns.—These valuable dyestuffs yield browns of specially pleasing tone and satisfactory fastness. The following recipe represents the method of dyeing a medium shade of cutch brown on pieces in a jigger:—

For 100 lbs. of goods use 50 lbs. of good extract cutch. Enter goods nearly at a boil. Add the colour in two ends; then add 5 lbs. of bluestone. Bring to a boil and boil one hour; shut off steam and allow to run from one-half to three-quarters of an hour. Draw off liquid and run in 2 lbs. of chrome. Run twenty minutes at 140° F. Rinse and dry. For a standing bath the amount may be reduced one-third. Gambier may be used in place of cutch and acts similarly.

For the toning of browns, fustic, bark, and flavine are available as yellows, and hypernic as a red. Logwood, sumac, and copperas can be used for darkening.

Two illustrations follow—a light bright brown dyed in a four-box machine and a dark brown dyed in a jigger.

Light Shade of Bright Brown.—Prepare gambier, bark, and chrome solutions at 10° Tw. The gambier and the bark are divided between the first two boxes. Use fifteen pails of gambier and nine pails of bark. The third box contains cold water and the fourth box the chrome. Use eight quarts of chrome liquor. After leaving the chrome bath the goods are well washed in a water mangle. Repeat the process. Dry and size.

Dark Brown.—Prepare a solution in the jigger containing for 100 lbs. of goods: 10 lbs. hypernic crystals, 5 lbs. logwood extract, 51° Tw.; 15 lbs. extract of fustic, 51° Tw.; and 15 lbs. extract of bark, 51° Tw. Add the colour in two ends. Boil one-half hour; shut off steam; add 1 lb. of bluestone. Run fifteen minutes. Add 2 lbs. chrome. Run fifteen minutes. Wash.

The use of logwood for blacks has so overshadowed the other natural dyestuffs that the thought of violets, oranges, reds, bright yellows, and blues does not come easily to mind when natural dyestuffs are mentioned. For this particular purpose the new mordant process is especially adapted. On the table, in addition to sample dyeings of the other processes described, are a range of bright fashion shades coloured by the new mordant process from natural dyestuffs.

In discussing this process earlier in the paper mention was made only of the ability of the new assistant to exhaust chrome on the fibre. This chemical is also able to fix other mordants—aluminium sulphate, tin crystals, copperas, and blue vitriol on cotton, and so firmly that washing will not strip the mordants. These mordants then react with the natural dyestuffs to produce a diversification of shades. Thus fustic on a tin or aluminium mordant produces brighter yellows than on a chrome mordant. Logwood on a tin mordant gives violet to Bordeaux shades of excellent brightness.

A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULPHUR IN RUBBER.*

By J. B TUTTLE and A. ISAACS.

Purpose of Investigation.

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulphur. Many investigators have worked on this subject, with the result that different laboratories have their own methods, and comparison of results obtained by these various methods is always difficult, and at times impossible.

This Bureau is now using in its routine analysis the method of Waters and Tuttle (Bureau of Standards, Reprint 174; *Journ. Ind. Eng. Chem.*, 1911, iii., 734). In order to learn whether or not the methods for this determination which have been recently published were an improvement, either in accuracy or time required, over the one now in use, and if not, to determine wherein these methods are faulty, this present investigation was undertaken.

General Consideration.

The determination of the total sulphur in rubber is far from being a simple problem, involving as it does the simultaneous determination of sulphur in a number of different substances. Sulphur may be found in vulcanised rubber compounds in any of the following forms:—

1. Free sulphur.
2. Sulphur combined with rubber (*i.e.*, vulcanised rubber).
3. Metallic sulphates, usually lead and barium.
4. Metallic sulphides, usually lead and zinc.
5. Sulphur compounds of fatty acids (from the so-called oil substitutes, or "factis").
6. Sulphur in bituminous substances ("mineral rubbers").

The first and second of these are always present, and the others may or may not be, according to the nature of the compound. Any method which has for its purpose the determination of the total sulphur must be adequate to determine any or all of these in widely varying amounts. In our experience in testing material for use in the Government departments, the total sulphur has varied from 1·5 to 25 per cent, the free sulphur from practically nothing to 10 per cent, and sulphur in metallic sulphates from nothing up to 6 per cent. The rubber content varied from 20 to 90 per cent, and the quality of the rubber varied from the best to the poorest. We have no quantitative data on the other sulphur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulphur.

The almost universal use of litharge (in amounts sometimes 15 and even 20 per cent) in rubber mixings may have considerable bearing on the determination of sulphur by some methods even though the litharge does not in itself contain sulphur. Its effect on the determination of total sulphur will be referred to later in the discussion of results obtained by the methods investigated.

Review of Recent Methods.

In connection with the previous publication on this subject from this Bureau (Waters and Tuttle, *loc. cit.*), a number of the methods in use at that time were investigated and discussed. Since then severel new methods have been proposed. Alexander's method (*Gummi Ztg.*, 1904, xviii., 729) involving the oxidation of the rubber with sodium peroxide was recommended by Allen ("Allen's Commercial Organic Analysis," 4th Ed., 1911, iv., 140) as a "reliable rapid method." Spence and Young (*Journ. Ind. Eng. Chem.*, 1912, iv., 413) worked on a variation of the electrolytic oxidation first suggested by Gasparini (*Gazz. Chim. Ital.*, [II.], 1907, xxxvii., 426), and afterwards developed by Hinrichsen (*Chem. Ztg.*, 1909, xxxiii., 735). Kaye and Sharp (*India Rubber Journal*, 1913, xliv., 1189) proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen (*Zeit. Angew. Chem.*, 1913, xxiv., 494) offered a new idea in an attempt to determine only the free sulphur and the sulphur combined with the rubber. After decomposition with concentrated nitric acid and evaporation, he treated the residue with sodium carbonate and water, and filtered, determining the sulphur in the filtrate colorimetrically. The Joint Rubber Insulation Committee (*Journ. Ind. Eng. Chem.*, 1914, v., 78) proposed a procedure for the complete analysis of rubber insulation material according to which the total sulphur is determined by fusion with a mixture of sodium peroxide and potassium carbonate. While this method was recommended for 30 per cent para insulation compounds only, it is desirable to know whether it has a wider application. H. P. Stevens (*Analyst*, 1914, xxxix., 74; *India Rubber Journal*, 1914, xlvii., 785) suggested a method for correcting for the loss of volatile sulphur in the Henriques method, by absorbing the gases from the determination in alkali, and subsequently determining the sulphur thus absorbed. Utz (*Gummi Ztg.*, 1914, xxviii., 631) gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald (*Ibid.*, 1903, xvii., 71). He considered the two methods of equal value.

There are two general methods for determining sulphur in organic compounds which have been used to determine the sulphur in rubber, viz., the Carius and the bomb methods. These are so well known that description at this time is unnecessary. Both of them are considered adequate to determine the total sulphur when modified to suit the conditions peculiar to rubber. Such modifications, however, are time consuming, and render these methods undesirable for the routine analysis of rubber goods. It was therefore not considered necessary to give analytical data in this paper.

Samples.

Even when the assumed total sulphur content is given, this information is not sufficient to enable one to judge the efficiency of the method, since some methods will give low results with materials containing much free sulphur. For the proper interpretation of the results by any method, the entire composition of the samples used, at least as far as the sulphur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in Table I. Sample A was one of the samples used in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G, and H were taken from deliveries on various Government contracts. (In this connection it will be of interest to note that G was taken from a delivery

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Table I.—*Composition of Samples.*

(The figures given are approximate percentages only).

Sample.	Description.	Rubber content.	Sulphur. Total.	Sulphur. Free.	Mineral fillers.
A	Insulation	30 Fine para	5·0	0·5	18 Barytes
B	Suction hose	40 High grade	6·0	0·5	18 Barytes
C	Special	48 Fine para	4·25 (*a*)	0·6	16 Barytes 16 Litharge
D	Insulation	28·5 Fine para	1·75	1·0	4 Litharge
E	Rubber bands ..	93 High grade	5·0	2·7	2 Litharge
F	Special	42 Coarse para	8·1 (*a*)	4	30 Sublimed lead 5 Litharge
G	Gasket	55 Poor quality	12·0	8	2 Barytes 2 Litharge
H	White tubing.. ..	20 Poor quality	21·0	9	36 Barytes

(*a*) The amount of sulphur added as such in Samples C and F was 2 per cent and 5·4 respectively.

Table II.—*Results of Tests for Sulphur.*

Method.	1. Spence and Young.			2. Deussen.			4. Joint Rubber Insulation Committee.	5. Kaye and Sharp.			6. Frank and Marckwald.	7. Waters and Tuttle.	8. Extraction with acetone.		
Sample.	Filtrate.	Residue.	Total.	Filtrate.	Residue.	Total.	Total.	Filtrate.	Residue.	Total.	Total.	Total.	Extracted.	Residue.	Total.
A	—	—	—	—	—	—	4·90	—	—	—	—	4·87	—	—	—
	—	—	—	—	—	—	4·94	—	—	—	—	—	—	—	—
B	—	—	—	4·53	1·66	6·19	6·26	3·63	2·43	6·06	6·00	6·29	0·51	5·74	6·25
	—	—	—	4·84	1·41	6·25	6·31	—	—	—	6·18	6·30	0·40	5·90	6·30
	—	—	—	3·84	2·74	6·58	—	—	—	—	6·26	6·33	0·44	5·85	6·29
	—	—	—	3·89	2·65	6·54	—	—	—	—	6·28	6·35	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	6·42	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	6·42	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	6·43	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	6·44	—	—	—
C	—	—	—	3·19	0·88	4·07	4·09	3·38	0·66	4·04	4·19	4·17	0·61	3·59	4·20
	—	—	—	2·55	1·52	4·07	4·13	2·45	1·68	4·13	4·20	4·18	0·63	3·60	4·23
	—	—	—	—	—	—	4·19	3·32	0·86	4·18	4·28	4·20	0·60	3·64	4·24
	—	—	—	—	—	—	4·31	—	—	—	—	4·22	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	4·23	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	4·25	—	—	—
D	—	—	—	—	—	—	1·73	—	—	—	—	1·65	—	—	—
	—	—	—	—	—	—	1·76	—	—	—	—	1·67	—	—	—
	—	—	—	—	—	—	1·78	—	—	—	—	1·70	—	—	—
	—	—	—	—	—	—	1·80	—	—	—	—	1·73	—	—	—
	—	—	—	—	—	—	1·81	—	—	—	—	1·75	—	—	—
	—	—	—	—	—	—	1·83	—	—	—	—	1·78	—	—	—
E	4·91	—	—	—	—	—	—	—	—	—	—	4·95	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	5·15	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	5·22	—	—	—
F	5·39	2·33	7·71	7·47	0·47	7·94	7·78	6·89	0·21	7·10	7·72	7·90	3·59 (*a*)	4·22	7·81
	6·90	0·88	7·78	7 74	0·22	7·96	7·80	6·81	0·38	7·19	7·78	7·96	3·26 (*a*)	4·81	8·07
	6·42	1·36	7·78	—	—	—	7·83	—	—	—	7·80	7·96	4·02	4·06	8·08
	5·04	2·75	7·79	—	—	—	8·01	—	—	—	7·86	7·96	4·04	4·04	0·08
	4·67	3·17	7·84	—	—	—	8·02	—	—	—	7·88	8·00	—	—	—
	5·05	2·81	7·86	—	—	—	—	—	—	—	—	8·01	—	—	—
	4·52	3·38	7·90	—	—	—	—	—	—	—	—	8·02	—	—	—
	4·71	3·26	7·97	—	—	—	—	—	—	—	—	8·09	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	8·11	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	8·12	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	8·12	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	8·13	—	—	—
G	11·49	0·35	11·84	5·52	4·04	9·56	10·98	9·89	0·04	9·93	11·56	11·96	8·31	3·69	12·00
	11·45	0·40	11·85	5·51	4·71	10·22	11·34	9·77	0·57	10·34	11·64	12·00	8·14	3·88	12·02
	11·46	0·39	11·85	8·33	2·81	11·14	12·04	9·80	0·55	10·35	—	12·04	8·06	3·97	12·03
	11·52	0·34	11·86	7·96	3·43	11·39	12·10	10·74	0·03	10·77	—	12·08	—	—	—
	11·36	0·53	11·89	—	—	—	—	10·42	0·41	10·83	—	12·16	—	—	—
	11·57	0·32	11·89	—	—	—	—	—	—	—	—	12·18	—	—	—
	11·43	0·47	11·90	—	—	—	—	—	—	—	—	12·19	—	—	—
	11·56	0·34	11·90	—	—	—	—	—	—	—	—	12·20	—	—	—
	11·47	0·45	11·92	—	—	—	—	—	—	—	—	12·23	—	—	—
	11·44	0·48	11·92	—	—	—	—	—	—	—	—	12·29	—	—	—
H	—	—	—	15·77	4·94	20·71	20·52	15·68	5·20	20·88	20·71	21·09	9·60	11·52	21·12
	—	—	—	15·69	5·16	20·85	20·68	—	—	—	—	21·16	—	—	—
	—	—	—	—	—	—	20·74	—	—	—	—	21·20	—	—	—
	—	—	—	—	—	—	20·83	—	—	—	—	21·30	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	21·32	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	21·36	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	21·40	—	—	—

(*a*) These samples were not completely extracted.

offered on a contract calling for 50 per cent fine para rubber, and not over 3 per cent sulphur other than that present as barytes). Sample D was prepared especially for the investigations of the Analytical Committee of the Rubber Section of the American Chemical Society. Samples C and F were specially prepared by one of the authors (J. B. Tuttle) at the factory of the Voorhees Rubber Manufacturing Co., at Jersey City, N.J., for the purpose of investigating the determination of total sulphur. Great care was taken in the weighing and mixing. The composition was chosen so as to show the effect upon the analysis of the two commonly used sulphates, barytes and sublimed lead, and the vulcanisation was controlled so that one of the samples should have a rather large free sulphur content. These two samples have practically the same composition as many that are frequently met with in our routine work, and may therefore be considered as representative of such materials.

Methods Compared.

Direct Solution Methods.—1. Spence and Young: Conc. HNO_3, fuming HNO_3, and electrolysis.

2. Deussen: Conc. HNO_3 and extraction with Na_2CO_3.

Direct Fusion Methods.—3. Alexander: Na_2O_2.

4. Joint Rubber Insulation Committee: Na_2O_2 and K_2CO_3.

5. Kaye and Sharp: ZnO and KNO_3.

Solution and Fusion Methods.—6. Frank and Marckwald: Fuming HNO_3, fusion with Na_2CO_3 and KNO_3.

7. Waters and Tuttle: Conc. HNO_3 and Br, fusion with Na_2CO_3 and KNO_3.

Special Method.—8. Acetone extraction, and separate determination of free and residual sulphur.

The methods as originally described by the various investigators were followed as closely as possible. Whenever it was considered advisable to depart from the original method, the reasons therefore are given. Unless otherwise stated, 0·500 grm. was taken for each determination. The "fusion mixture" used was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters (*Journ. Ind. Eng. Chem.*, 1913, v., 853). The barium sulphate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. Insoluble residues were examined for sulphur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found to be practically free from sulphur, so that no corrections are necessary on their account. Methods 4, 6, 7, and 8 are intended to determine the total sulphur, while 1, 2, 3, and 5 are intended for the determination of sulphur other than that present as insoluble sulphates.

1. *Spence and Young.*—The rubber was treated with 5 cc. of concentrated nitric acid, and heated gently. When the first reaction was over, about 50 cc. (exact amount was not specified by the authors) of fuming nitric acid were added, and the solution electrolysed. As a source of current, an 8-volt storage battery was used. This was connected directly to the platinum electrodes. The resistance of the electrolytic cell was such that the current was usually between 2 and 3 ampères, though at times it was as low as 1 ampère. After two or three hours the current was discontinued, the electrodes removed, 1 grm. of potassium nitrate (see Note) was added, and the solution evaporated to dryness. The nitric acid was completely removed with hydrochloric acid by several evaporations. A few drops of hydrochloric acid were added, the residue was treated with hot water, and filtered. The sulphur in the filtrate was precipitated as usual. The insoluble matter filtered of above was fused with 5 grms. of fusion mixture, extracted with hot water, filtered, and after acidification the sulphur in the filtrate was precipitated as usual.

(Note.—Spence and Young add 1 grm. of sodium carbonate, but, inasmuch as this on solution is changed to sodium nitrate, we used potassium nitrate, which serves the same purpose and obviates the spattering caused by the addition of a carbonate to the hot concentrated acid).

2. *Deussen.*—The Deussen method was not followed exactly as given by the author. The rubber was treated in a porcelain crucible with concentrated nitric acid, and covered. After heating for a short time the cover was removed and the solution evaporated to dryness. The residue was treated with sodium carbonate and water, and after heating the solution was filtered. Up to this point the original method was followed exactly. Deussen reduces the sodium sulphate to sulphide, and determines the latter colorimetrically. In order to avoid any error introduced by this procedure and to obtain a better comparison with the other methods, we added potassium nitrate to the filtrate, evaporated to dryness, and fused. The sulphur in the cooled melt was determined as under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grms. of fusion mixture and the sulphur determined as usual.

3. *Alexander.*—The Alexander method, as given in "Allen's Commercial Organic Anaylsis," is said to be rapid and reliable. The rubber is intimately mixed with 16 grms. of sodium peroxide in an iron crucible provided with a lid through which a small hole has been bored. The combustion is started by introducing through this hole a red-hot iron wire. No further heating is required. When the mass is cooled it is dissolved in water, the crucible, lid, and wire are removed, the solution is acidified with hydrochloric acid and boiled, then filtered if necessary, and the sulphate precipitated by means of barium chloride.

4. *Joint Rubber Insulation Committee.*—The rubber was fused with 4 grms. of sodium peroxide and 6 grms. of potassium carbonate. The cooled melt was extracted with hot water to which some bromine water had been added, The solution was filtered, acidified with hydrochloric acid. and evaporated to dryness to dehydrate silica. About 400 cc. of water were added, the solution made slightly acid with hydrochloric acid, filtered, and the sulphur in the filtrate determined as usual.

5. *Kaye and Sharp.*—The rubber was mixed with 4 grms. of zinc oxide and 2 grms. of potassium nitrate, placed in a crucible (both iron and porcelain were used), and covered with a layer of zinc oxide about 1 cm. deep. This was carefully heated, at first with a low and afterwards with a full Bunsen flame. The crucible and contents were placed in a beaker, covered with water, and heated; the solution was acidified with hydrochloric acid, and filtered. The sulphur in the filtrate was determined as usual.

The insoluble residue filtered off from the hydrochloric solution was fused with 5 grms. of fusion mixture, and the sulphur determined as under the insoluble matter in the Spence and Young method.

6. *Frank and Marckwald.*—The rubber was treated with about 20 to 25 cc. of fuming nitric acid in a porcelain crucible, the vessel covered with a watch-glass, and allowed to stand over night. The solution was evaporated to dryness, the residue fused with 5 grms. of fusion mixture, extracted with hot water, and filtered. The filtrate was acidified with hydrochloric acid and the sulphur precipitated as usual.

7. *Waters and Tuttle.*—The rubber was treated in a porcelain crucible with 25 cc. of concentrated nitric acid saturated with bromine, the vessel covered with a watch-glass, and allowed to stand one hour. It was heated on a steam-bath for one hour, and then the cover was removed and the solution evaporated to dryness. The residue was fused with 5 grms. of fusion mixture, extracted with hot water, filtered, the filtrate acidified with hydrochloric acid, and the sulphur precipitated as usual.

8. *Extraction with Acetone.*—Some determinations were made by extracting 2 grms. of rubber with freshly distilled acetone for eight hours. The acetone solution was evaporated to dryness, distilled water and bromine added, the solution heated until colourless, filtered, and the sulphur in the filtrate determined as usual. The insoluble residue

was examined for sulphur by fusing with 5 grms. of fusion mixture. The amount of sulphur thus found was scarcely ever more than a few tenths of a mgrm.

The extracted rubber was dried at about 60° C. and the sulphur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulphur.

Discussion of Results.

Although the method of Waters and Tuttle is No. 7, it has been considered advisable to discuss it first, since it is the most reliable and accurate method we have found for the determination of total sulphur. The reaction proceeds slowly without any very great evolution of heat, so that there is little or no chance of losing free sulphur. Even when the free sulphur is very high the method is adequate to determine it with accuracy. A large number of determinations were made, and the results are concordant and agree with the calculated results in samples of known composition.

The Waters and Tuttle method has been in use at the Bureau of Standards for a number of years, and during that time has frequently been used in determining the total sulphur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods which have been compared in the course of this investigation may be divided into two classes, viz., those for the determination of the total sulphur, and those for the determination of sulphur other than that present in the insoluble sulphates. They may be further classified according to the method of attack employed, as follows:— Direct solution, direct fusion, and solution and fusion methods.

The methods which have for their object the determination of sulphur other than that present in the insoluble sulphates (Nos. 1, 2, 3. and 5), attempt to separate the insoluble sulphates by filtration. Spence and Young, Alexander, and Kaye and Sharp filter from an acid solution. The securing of correct results by this method is based upon the obviously incorrect assumption that the lead sulphate originally present would remain insoluble, while that formed from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulphate will react with sodium carbonate solution with the formation of soluble sodium sulphate. It is apparent, therefore, that such methods cannot give reliable results since their basic principles are faulty.

Considering the methods as classified according to the mode of attack, we find that the direct solution methods (Nos. 1 and 2) employ concentrated nitric acid. The use of this reagent in the determination of the total sulphur in rubber was first suggested by Henriques, and many investigators have shown that its use gives low results, probably on account of the loss of free sulphur. Even when the sulphur which is remaining in the insoluble residue is included with that in the filtrate, the sum does not equal the calculated value.

The direct fusion methods (Nos. 3, 4, and 5) give results which are satisfactory only when the free sulphur content is relatively low. In view of the results obtained by the other fusion methods, it was not considered necessary to make any determinations by the Alexander method. The reaction between rubber and sodium peroxide often proceeds with explosive violence, particularly so when, as in this method, the sodium peroxide is not diluted with some less active flux. The more important points have been demonstrated by the results on the other methods, namely, (1) that the direct fusion may give low results, and (2) that the filtering of the solution of the melt after the addition of acid gives results which have no relation to the sulphur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by an explosion, the results show that it is open to all the other objections which have been made above; hence it cannot be relied upon to give results which have any significance.

The results obtained by the method of the Joint Rubber Insulation Committee (No. 4) are accurate when the free sulphur is low, as it is in insulation compounds, so that it may be relied upon to do all that this Committee has claimed for it. This has been also substantiated by the work of the Analytical Committee of the Rubber Section of the American Chemical Society (*Journ. Ind. Eng. Chem.*, 1914, vi., 514). Whenever the free sulphur content is high our results indicate that this method has the same serious defect as the other direct fusion methods.

The methods which require both solution and fusion yield the most satisfactory results. One of these (the Waters and Tuttle method) has already been referred to. The Frank and Marckwald method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulphur. The reaction between the rubber and the fuming nitric acid is at times very violent, and considerable heat is evolved. In fact, in several cases by adding only 1 or 2 cc. of the acid the heat was so great as to cause the rubber to take fire. It seems probable that this heating is responsible for the loss of sulphur and the consequent low results.

In view of the fact that the free sulphur can be determined by several methods (one of which has already been described) with considerable accuracy in the acetone extract, and since this determination is usually made in analyses of vulcanised rubber goods it is possible, and in some cases may be convenient, to determine the total sulphur by adding to the result for free sulphur the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulphur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total sulphur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulphur remaining in the rubber after the acetone extraction by the Waters and Tuttle method. It is more than possible that other methods will be equally efficient.

Outline of the Method Adopted by the Bureau of Standards.

As the result of this and other investigations and the experience of the Bureau of Standards, extending over some years, we believe that the Waters and Tuttle method is the most reliable, and it has been adopted for use in the routine work there. The determination is made as follows:—

Half a grm. of rubber is placed in a porcelain crucible of about 100 cc. capacity, 20 to 25 cc. of concentrated nitric acid which has been saturated with bromine, are added, the crucible covered, and allowed to stand for one hour. It is then heated gently for one hour, after which the cover is removed, rinsing it with a little distilled water, and the solution is evaporated to dryness.

Five grms. of fusion mixture (1 potassium nitrate to 1 sodium carbonate), and 3 or 4 cc. of distilled water are added, the mixture is digested for a few moments on the steam-bath, and then spread halfway up the side of the crucible to facilitate drying. The drying is done on a steam-bath or electric hot plate; in the latter case care is taken to avoid spattering caused by possible overheating. When dry the mixture is fused over a sulphur-free flame until all the organic matter has been destroyed and the melt is quite soft. The crucible and contents are cooled, placed in a 600 cc. beaker, covered with distilled water, and heated on the steam-bath for three or four hours. The solution is then filtered, and the insoluble matter washed thoroughly. The combined filtrate and washings should amount to about 500 cc. About 7 or 8 cc. of concentrated hydrochloric acid are added, the beaker covered, and the solution heated almost to boiling. The solution is now tested, and if necessary made slightly acid toward Congo paper; if the directions have been followed exactly there should be a slight excess of acid present. Ten cc.

of 10 per cent barium chloride solution are added, and the solution is allowed to stand over night. The precipitated barium sulphate is filtered off and ignited over a small Bunsen flame, care being taken to see that the filter-paper does not inflame. The barium sulphate is calculated to sulphur by means of the factor 0·1374.

Summary.

It is shown that the methods which have been proposed for the determination of the total sulphur other than that present as insoluble metallic sulphates are not satisfactory.

It is shown that loss of sulphur is likely to occur in the direct fusion methods, and this loss is apt to increase with increasing free sulphur content.

The method of Waters and Tuttle is recommended for the determination of total sulphur. This method is accurate and comparatively rapid, and has given satisfactory results in the hands of a number of analysts over a rather extended period of time.

A new suggestion is offered, namely, to determine separately the free sulphur and the sulphur remaining after the acetone extraction, reporting the sum of the two quantities as the total sulphur. This procedure eliminates the troublesome effect of the free sulphur upon the determination of the total sulphur.

The authors wish to express their appreciation of the many suggestions made by Dr. C. E. Waters, of this Bureau, and of the assistance given by the Voorhees Rubber Manufacturing Co., of Jersey City, in permitting us to make up some compounds of known composition in their factory.

A PLEA FOR A CHEMISTS' PROTECTIVE ASSOCIATION.*

By ROLLIN G. MYERS.

(Concluded from p. 84).

Relation of Business Man to Chemist.

To be more particular, the valuation at which the business man rates the chemist is based on amounts paid to chemical employees by other business men. But can the business man judge rightly in respect to a just wage for the chemist? He certainly cannot, for he has no particular training in chemistry and but little understanding of the high quality of the work which the chemist must do to get the proper results. It is hardly possible, then, for the business man to arrive at correct conclusions regarding the proper rating of the chemist's work. *Would not the business man employ similar arguments if the positions were reversed and the chemist decided the financial return for business men?* And right in line with the statement that a chemist is worth only so much, this thing suggests itself—Suppose that ten years from now, due to a successful solution of the wage problem, the salaries of chemists had been increased materially, would not the business man say, as he does now, that the chemist is worth only so much? Is it not true, after all, that the commercial valuation of the workers largely depends on the mental and physical pressure they can exert on their employers? The average worker cannot press his demands to any great extent, and whatever increase he receives is largely governed by the caprice of those above him; hence the need of organisation. The trade unions resulted undoubtedly from the entirely selfish and tyrannical attitude of the business representatives of capital towards labour. Before the advent of the unions business men settled the wage scale to suit themselves. Frequently a high-handed policy was pursued. Conditions are different now in this respect, for the business man finds it to his best advantage to consult with the officials of the unions over any prospective changes in wages. It is true that the unions at times have abused their power, but the same statement holds true for the employers of labour. From the writer's point of view both are necessary in the social organisation and both rightly have a voice in the settlement of a question which reacts so profoundly on society. But if untrained labour has a voice in determining a just wage for itself, who shall say that trained labour, in this case chemical labour, should not demand an equal place in the sun? *Is the struggle for existence any the less hard for the chemist at an equal or less salary than for the labourer?* Perhaps the business man has become deluded into the idea that the chemist is not so necessary to the success of a company or corporation as common labour. If the chemists and chemical workers of the U.S. Steel Corporation or the Swift Packing Company suddenly stopped working could these organisations still operate? It would seem very doubtful. But assuming that they could adjust themselves to the altered conditions could they successfully compete with the rival companies employing chemists? In this age it would be impossible. And what would it mean from the financial side? It would mean the daily loss of thousands of dollars. What would be the effect on common labour? A partial or complete laying off of those employed. If there is any doubt, let the officials of any company or corporation employing chemists try the experiment for a month without them. To say the least, these possibilities are well worth considering by the business men as well as the chemist.

The writer's aim is not to antagonise business men, except perhaps in asseverating that their attitude to the wage of the chemist is wrong and unprogressive. It is true they often tacitly or expressly admit that the wages are low by promising an increase in salary shortly, either from greater efficiency or promotion. So, too, the promise is often fulfilled, but the increase in salary is so small and diminishes so rapidly in its approach to the average wage set by business men that the chemist realises acutely after several years of hard work that he has barely made a living; in fact if he is at all cynical he concludes that in some manner he has been tricked and deceived. Even in respect to promotion the extra compensation received is hardly ever commensurate with the added responsibility for the accuracy of thousands of determinations or for the quality of some marketable product. Neither should we at any time lose sight of the fact that many chemists lack the executive capacity for head positions as well as the particular ambition for them. But to contend on aceount of this that the efficiency of these workers is reduced and their value is lessened as well as their earning power is decidedly wrong. To say the least, it indicates a very selfish way of looking at things. The chemist in a subordinate position who does his work carefully and conscientiously is deserving of so much financial return that he, as well as his chief, can obtain enjoyment without unduly skimping himself, and at the same time properly maintain his professional standing.

Low Standards in Technical Laboratories.

While the one-sided policy of business men in fixing the wage of chemists has been given the *greatest* weight among causes producing low wages, there are two others, it is believed, which also favour the same effect. One of these is the ease of obtaining positions in technical laboratories, since in most cases nothing is required of the applicant save an ability to learn a few rapid technical methods. The time of apprenticeship is short, and in a few weeks the former applicant becomes a laboratory automaton, capable of turning out the required results. Later perhaps this "would-be chemist" hears of a better position. He applies, and frequently, by means of credentials from his chief, obtains the situation. If he takes charge of a laboratory he, also, eventually needs an assistant. Sometimes a chemist is selected, or, as before, some boy or untrained person is broken in. The general trend of this policy is to supplant chemists by untrained workers. The personnel of the profession suffers in consequence, and this in turn has a detrimental effect on the wage, as was previously pointed out. There is another aspect also from which this condition of affairs may be viewed. It is in respect to the law of supply and demand. The increased number of persons in the chemical field, due to the continual influx of untrained workers, may produce such a supply of applicants for chemical positions that the demand is equalled or exceeded. This condition would again tend to a reduced wage. The greater sufferer is always the chemist, not only from the lessened return of his four or more years of hard training, but of the money he invests for his training as well. Perhaps the chemist himself can be blamed to a certain extent for these conditions. At least he has been decidedly short-sighted in not maintaining the high standard of his subordinates by insisting on trained assistants, even in the face of the aggressive attitude of his employer against any increase in expenditure. Still, the business man has set the precedent and can exert the greater pressure, so that the chemist is handicapped in most instances. The business man has also shown a short-sightedness in not realising the superlative value of the chemist in any respect over the untrained man.

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* Presented before the Louisiana Section of the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 9.

Responsibility of Teachers of Chemistry.

The other cause referred to is the sceptical state of mind common to many professors of chemistry in technical schools and universities respecting any increase in the average wage of chemists. Many of them sincerely deplore this condition of affairs, but beyond this they do not go. Whether they reach the conclusion that any amelioration is impossible, or that in any case the chemist will successfully adjust himself to an unsatisfactory environment, does not relieve these men from a certain share of responsibility for the future welfare of their student graduates. The intellectual and ethical standard of the heads of the various chemical departments is admirable. Their lofty ideals and their inspiration in widening the sphere of chemical knowledge by investigation and research have the profound effect of advancing science and of improving social life as well. In view of the elevated standing of these men they could have great moral influence in bringing about a change of attitude in business men, which would be decidedly favourable to an increase of emolument for the chemists. The student graduates and other chemists could be impressed also with the necessity of encouraging only those applicants for chemical positions whose training justly entitled them to become members of the profession.

Proposed Plan for Protective Association.

The power to effect changes of moment for the betterment of the individual is obtained only by the close association and the concerted agreement of the many in respect to formulated and definite policies of action. The objective manifestation of this principle is easily seen in the promotion and existence of protective associations for practical ends and of societies for social and speculative purposes. In the discussion so far the writer has shown the imperative need of a protective association for chemists by pointing out the small wage paid to these men, the low personnel, and, what is more convincing, the inability of a chemist alone to remove the causes which actively produce the unsatisfactory conditions. A protective association, then, is the only remedy which has a recognised potency over the evils discussed. According to the principle enunciated its functions must be directed by definite and formulated policies. In respect to wage it must decide on a just emolument for chemists, to be regulated by the character of the work, the rank and experience of the worker, as well as by a proper regard for the rights of the employer and business man. The length of the working day and the extra fees for work overtime, at night and on holidays, should be settled also. In respect to personnel, a *protective association should limit its membership to chemists*, though a special concession might be granted to quasi chemists with at least three years' chemical training in a technical school or university. To distinguish them from the graduate members they could be called "chemists by courtesy." In addition the applicants for positions in practical laboratories should be sharply limited to two classes—(1) chemists; (2) quasi chemists who have at least three years of a *bona fide* chemical training, and who must pass a compulsory examination over the principal branches of chemistry.

By firmly maintaining the stand taken as to the wage and the personnel, a protective association could widen its policies eventually and take on other functions, the following of which may be suggested:—(*a*) To keep an up-to-date register of the chemical laboratories and of the chemists in the United States; (*b*) to keep a daily register of all members seeking positions and to keep them promptly informed of any actual and prospective vacancies in chemical laboratories; (*c*) to aid the applicant for a position in every way possible; (*d*) to keep a careful watch on the supply of chemists and the demand for them, in order to control as efficiently as is possible any excessive increase or decrease of applicants by influencing the heads of chemical departments to encourage or discourage students in the study of chemistry when the occasion demanded this; (*e*) to take aggressive action against all companies or corporations which are unjust and unfair to chemists; (*f*) to assume a critical attitude to all chemists who through personal ambition of a mercenary character or in any other way seek to lower the profession and defeat the policies of the association; (*g*) to assist financially when possible all members of the association who have been temporarily or permanently incapacitated through sickness, accident, or age.

The policies and functions outlined for a chemists' protective association may be looked upon as parts in a working formula. The supposition that its application will bring about a decided improvement in the financial returns, besides elevating chemistry to its just place among the other professions, is strengthened greatly by two classes of facts.

I. From the standpoint of wage, we have seen the large increase in financial return by the many kinds of untrained labour after organisation.

II. From the standpoint of personnel we know that practising physicians, dentists, pharmacists, and lawyers are limited to those who can pass satisfactory examinations given by the State. It is hardly necessary to add that those applicants who pass the examinations have had several years of training in universities, where they have received degrees. In Germany the "Verband Deutscher Chemiker" (the German Chemists' Association) exists, which limits the applicants for positions in chemical laboratories to those who can pass satisfactory examinations and who have degrees.

Organisations, whether for trained or untrained labour, consciously or unconsciously limit their membership to those who represent the best in the field. In so doing the personnel is raised, and this in turn reacts favourably to an increase in wages. There is one thing more—the fact that organisations have clear and definite policies and stand for certain desired ends produces a profound impression on the public mind. The masses learn to associate certain practical gains with the principles peculiar to a trade or a profession. This means an education of the public and the great moral effect of a favourable sentiment to the just objects of an association.

In respect to the adoption of ways and means required to launch successfully a protective association for chemists the following suggestions are advanced:—(*a*) Let the American Chemical Society or the Chemists' Club of New York make a careful canvas of the actual number of chemists in the United States, their rank, their salaries, and the companies they are connected with; (*b*) let a straw vote be taken of all the listed chemists in respect to their desire for a protective association; (*c*) have a printed statement, which describes and fixes the functions of the association, the salaries and the standard for applicants for positions in practical laboratories, sent to all chemists, and their comments and suggestions encouraged (this statement to be formulated by a committee of the members of the association which acts favourably on the ideas set forth in this paper).

In conclusion, the writer believes that he has not only shown the need of a protective association for chemists, but he has also shown that it will accomplish all that is necessary in improving the practical conditions of the chemists in this country. If it is argued that there is a certain humiliation for chemists in establishing an association similar to those of untrained labour, it should also be considered *that it is more humiliating* to work for a salary frequently less than that received by untrained labour, and to compete with chemical workers whose training is deficient, who have paid nothing for an education, and who have taken positions justly belonging to chemists.

Finally, the writer ventures the hope that the chemists of the United States will see fit to take up the idea of practical organisation, and that in not so many years the chemical profession will stand even with the highest, not only in respect to a just compensation received for services but also to the personnel of its members.

THE CARBOHYDRATES AND THE ENZYMES OF THE SOY BEAN.*

By J. P. STREET and E. M. BAILEY.

(Concluded from p. 82).

Cell Wall Constituents.

One per cent Hydrochloric Acid Extract.—The residues from the starch determinations were thoroughly washed with water, alcohol, and ether, and dried. At this stage all the more readily soluble sugars and the starch have been removed, and there remain the cell wall constituents, viz., true cellulose and those complex substances closely related to cellulose and collectively termed "hemicelluloses." The hemicelluloses are less resistant to dilute acids than true cellulose, and they yield copper-reducing bodies of the hexose and pentose types. It is here that the true pentosan and galactan are found. In the soy bean Schulze (*Journ. Phys. Chem.*, 1890, xiv., 253) has shown that the hemicelluloses give rise to the pentose sugar arabinose and the hexose galactose.

The above residue from the malt digestion was accordingly boiled with 1 per cent hydrochloric acid for one hour under a reflux condenser—this acid having been found to be very effective in hydrolysing pentosans (Councler, *Chem. Ztg.*, 1894, xviii., 1617). The solution was then filtered, the residue washed with hot water, the filtrate neutralised, cooled, and made up to a definite volume. An aliquot equivalent to 0·4 grm. of the fat-free and alcohol-extracted substance reduced 0·0801 grm. of Cu_2O, equivalent to 0·0345 grm. of dextrose, or 5·93 per cent in the original material. As stated above, this reduction is not due to dextrose but to the combined action of arabinose and galactose. With the data obtained up to this point we cannot say in what proportion these sugars are present. Their reducing powers, according to Browne's experiments (*Journ. Am. Chem. Soc.*, 1906, xxviii., 439), are—

$$\frac{\text{glucose}}{\text{arabinose}} = 1·032, \text{ and } \frac{\text{glucose}}{\text{galactose}} = 0·898.$$

Calculating the reducing power obtained above as due entirely to arabinose we obtain 5·75 per cent, or as due entirely to galactose, 6·60 per cent. It is seen that expressing the results as "sugars due to hydrolysis of hemicelluloses as dextrose" gives a figure close to the mean.

In order to gain data for the more definite expression of the copper-reducing substances obtained at this stage of the analysis, determinations of galactan and pentosan were made.

Galactan.—Another residue from malt digestion was oxidised with nitric acid as in the official method for total galactan. A yield of 0·1480 grm. of mucic acid (m. p. 212—214° C., r. h.) was obtained, equivalent to 3·38 per cent of galactose, or 3·05 per cent of galactan on the original basis.

Pentosan.—A third residue from the malt digestion was treated in the usual way for furfurol-yielding substances, the equivalent of 3·09 per cent of pentosan, or 3·37 per cent araban, being found.

Thus it appears that galactan and pentosan are present in practically equal amounts, and therefore the reduced copper can best be expressed on the basis of the mean specific reducing powers of galactose and arabinose. Calculating in this way we obtain 6·18 per cent of carbohydrate which is due to a galactoaraban complex. This percentage agrees closely with the sum of the percentages of galactan and araban as determined.

1·25 *per cent Sodium Hydroxide Extract.*—The residue from the hydrochloric acid treatment was then boiled for thirty minutes with 1·25 per cent sodium hydroxide solution, the filtrate being neutralised and hydrolysed for two and one-half hours with hydrochloric acid. This filtrate was shown to have no copper reducing power.

Crude Cellulose.—The residue from the previous treatment was thoroughly washed with water, alcohol, and ether, and dried. It weighed 0·2065 grm., equivalent to 3·55 per cent on the original basis (not corrected for ash).

True Cellulose.—This residue was then moistened with water and exposed to chlorine gas for one hour, then washed with water, boiled in a solution of 2 per cent sodium sulphite and 0·2 per cent sodium hydroxide, filtered, washed, and dried. The residue from this treatment weighed 0·1945 grm., equivalent to 3·34 per cent on the original basis (not corrected for ash). The ash of this residue weighed 0·0027 grm., or 0·05 per cent on the original basis, making the true cellulose 3·29 per cent.

Distribution of Pentosans and Galactans.

Distinct from the insoluble hemicelluloses of the cell wall constituents are the soluble pentose- and hexose-yielding substances. In this group, broadly termed saccharo-colloids by Tollens, belong the vegetable gums and mucilages, which, from the nature of their transformation products, must be regarded as pentosans and galactans. They are soluble in water and generally insoluble in strong alcohol, though some appear to be dissolved to a slight degree in the latter solvent, especially if somewhat dilute. It should not be forgotten, of course, that certain true sugars yield mucic acid and furfurol due to some particular complex in the sugar molecule. Thus raffinose yields mucic acid and sucrose yields furfurol, due to the galactose and lævulose complexes respectively.

According to Schulze water-soluble pentosans are present in small amount in the soy bean. We have endeavoured to gain some idea of the distribution of pentosan and galactan by determining the mucic acid, and furfurol yields in the hot alcohol-extracted and in the water-extracted and malt-digested residues.

In respect to mucic acid-yielding substances the total galactan found was 4·86 per cent. In the alcohol-extracted material 4·62 per cent was present, and in the water-extracted and malt-digested residue 3·05 per cent. It appears therefore that a small amount of the mucic-acid yielding substance was removed by hot 95 per cent alcohol. This is attributable to the galactose complex in the raffinose molecule. Extraction with water and digestion with malt removes 1·57 per cent, showing that galactose arising from water-soluble galactan was in part responsible for the copper-reducing power of the hydrolysed water extract already noted. There remains 3·05 per cent, or 62·7 per cent of the total galactans, in the cell wall constituents.

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* *Journal of Industrial and Engineering Chemistry*, vii., No. 7.

With regard to pentosans there were found in the original soy bean meal furfurol-yielding substances equivalent to 4·94 per cent pentosan. Hot alcoholic extraction removed 0·83 per cent, and 1·02 per cent was removed by treatment with water and by malt digestion. Thus 3·09 per cent, or 62·5 per cent of the total pentosan, remains in the cell wall constituents. The small amount removed by alcohol is largely due to substances insoluble in water, precipitated or occluded in the lead precipitate, when the alcoholic extract is taken up with water and treated with basic lead acetate. This lead precipitate was found to yield copper-reducing matter equivalent to 0·5 per cent pentose. The nature of the saccharo-colloids is rather obscure, but they are quite probably the vegetable gums and mucilaginous materials present in seeds and plant tissues, which are dissolved in a slight degree by alcohol, and which are removed more completely by water in the next stage of our analysis. The removal of fructose as such, or in complex, may also offer a partial explanation. The 1·02 per cent of pentosan removed by water contributed to the copper-reducing power of the hydrolysed water extract.

Organic Acids.

Organic acids are largely precipitated by lead acetate, and the attempt was made to determine these by the scheme outlined by Schulze, viz., precipitating the aqueous solution of the alcohol extract with lead, removing the excess of lead, decomposing the lead precipitate with hydrogen sulphide, removing the excess of the latter, and then precipitating the acids with calcium or strontium. An attempt to precipitate these acids with calcium acetate, as is done in the case of malic acid, failed for some unknown reason. Strontium hydroxide, however, gave uniform results, but somewhat lower than expected, although there are no recorded analyses for comparison. The lead precipitate from 50 grms. of material was decomposed with hydrogen sulphide, and the excess of the latter removed from the filtrate by evaporation. The clear white solution was made up to 500 cc. and aliquots of 50 cc. taken for analysis. The aliquots were evaporated to 20 cc., 2 to 3 cc. of a saturated solution of strontium hydroxide, and 180 cc. of 95 per cent alcohol were added, and the mixture was heated on the steam-bath for one hour, then filtered while still hot. The precipitate obtained was yellowish in colour, the filtrate being clear and giving no further precipitation with additional strontium hydroxide. On igniting the precipitate and titrating the strontium oxide 1·44 and 1·29 per cent of organic acids, calculated as citric, were obtained.

Undetermined Substances.

The amount of nitrogen-free extract which remains unaccounted for is 8·60 per cent. This is attributed largely to those undetermined substances removed by alcohol, since there was obtained about 16 per cent of alcohol extractives of which a little more than one-third have been determined. The exact nature of the undetermined extractives cannot be stated with much certainty, but they undoubtedly include chromogenic substances, vegetable waxes, and possibly tannin complexes. It has already been noted that basic lead acetate produced a voluminous precipitation of these alcohol-soluble materials, but the purpose of this investigation has been served in demonstrating to what extent they were copper-reducing or yielded copper-reducing bodies on hydrolysis. It has been shown that the amount of such substances was small. We shall include these undetermined extractives in the alcohol fraction through lack of data for their distribution.

Summary.

A consideration of the above data shows that the meal examined contained 4·51 per cent total sugars, 0·50 starch, 3·14 dextrin, 4·94 pentosan, 4·86 galactan (less 0·24 due to raffinose), 3·29 cellulose, 1·44 organic acids, and 8·60 per cent waxes, colour principles, &c. Of these constituents only the first three, viz., the sugars, starch, and dextrin, amounting to 8·15 per cent, may be considered objectionable in a strict diabetic diet. The remaining nitrogen-free extract, 22·93 per cent, about three-fourths of the whole, consists of pentosans, galactans, organic acids, waxes, &c., forms which are not generally considered a source of danger in a diabetic diet (Table III.).

Table III.—*Summary of Analysis of Nitrogen-free Extract and Fibre.*

Hot 95 per cent alcohol extract—	
Insoluble in water or precipitated by lead acetate :	
Saccharo-colloids as pentosan	0·83
Organic acids, as citric	1·44
Waxes, colour principles, &c., by difference	8·60
Soluble in water and not precipitated by lead acetate :	
Invert sugar	0·07
Sucrose (Creydt)	3·31
Raffinose (Creydt) (0·24 galactan derived from galactose complex in raffinose)	1·13
Cold water extract—	
Soluble starch	0·00
Reducing matter after hydrolysis, calculated as dextrin (including 1·57 galactan and 1·02 pentosan)	5·73
Malt extract—	
Starch	0·50
1 per cent hydrochloric acid extract—	
Hemicelluloses, reducing matter calculated as galacto-arabinose (determined directly in the malt residue, galactan 3·05, pentosan as araban 3·37	6·18
1·25 per cent sodium hydroxide extract—	
Reducing sugars	0·00
Chlorinated residue, true cellulose	3·29
Total	31·08

The Enzymes of the Soy Bean.

A number of investigators have reported the presence in the soy bean of various enzymes. The most conspicuous and important is the urease of Takeuchi (*Journ. Coll. Agr. Univ. Tokyo*, 1909, i., 1), which acts specifically upon urea, liberating ammonia. He has called attention to the economic possibilities of this enzyme from an agricultural standpoint, and Van Slyke and others (*Journ. Biol. Chem.*, 1914, xix., 2) have made practical analytical use of it in the form of standardised urease preparations for determining nitrogen in urea-containing substances, such as blood, urine, and other animal secretions and juices. Stingl and Morowski have reported the presence of a powerful amylase (*Monatsh. Chem.*, April, 1886). Bertrand and Riokind discovered a glucoside, vicianin, and an enzyme capable of effecting its hydrolysis. (*Bull. Sci. Pharm.*, 1907, xiv., 161).

In this examination of soy bean meal a number of additional enzymes have been found. They will be mentioned only very briefly, since the wide distribution of enzymes in seeds and other vegetable tissues and the readiness with which they can in most cases be detected, make a survey of such materials for the detection of enzymes of decreasing interest. The meal was ground with sand and distilled water, the suspension filtered through cheese-cloth, and the turbid filtrate used in most of the trials recorded.

Amylase.—An aliquot representing 1 grm. of material completely transformed 0·1 grm. of soluble starch in three hours at 55°, while with 0·1 grm. of material acting on an equal weight of substance the transformation reached the erythrodextrin stage as indicated by iodine tests.

Sucrose.—Polariscopic readings indicated no hydrolysing action upon cane-sugar. Turbid filtrates and direct suspensions of the meal in water were allowed to act upon a N/2 solution of sucrose for periods of time up to eighteen hours at temperatures ranging from 20° to 55°.

Protease.—No gelatin-liquefying action was detected, but in trials with Witte peptone at 40° and with HCN as the antiseptic positive tryptophane tests were obtained after forty-eight hours, the same being very marked after seventy-two hours. Trials in which the peptone was omitted gave negative tryptophane tests, indicating no action upon the native proteins of the soy bean itself.

Oxidases.—Water suspensions of the meal decomposed hydrogen peroxide slowly at room temperature. They were without effect upon tincture of guaiacum except in the presence of hydrogen peroxide, when a blue coloration was rapidly produced.

Lipase.—There is a distinction between those enzymes capable of decomposing various esters (butyrases) and the true lipases which act upon the natural fats. The soy bean was found to effect both of these reactions. True lipases have been found in the seeds of Ricinus, rape, opium poppy, hemp, flax, and maize, and are presumably present in all oily seeds.

The first trials made were with the turbid filtrate prepared as described above. The substrate used was butyrin (Merck's) and the antiseptic toluol. Portions equivalent to 1 grm. of material were allowed to act on 0·25 cc. of butyrin at 40°, all trials being neutralised to phenolphthalein at the beginning, and the acidity subsequently developed determined by titration with N/10 sodium hydroxide at 24-hour intervals. The duration of the experiment was ninety-six hours. The results can best be expressed by a tabulation of some typical trials and their controls (Table IV.).

Table IV.—*The Action of Soy Bean Preparation with Butyrin.*

Solutions tested. (Toluol added to all).

No.	Butyrin.	Water.	Addition.
1.	0·25 cc.	20 cc.	—
2.	None	None	20 cc. extract
3.	0·25 cc.	None	20 cc. extract
4.	0·25 cc.	None	20 cc. *boiled* extract
5.	0·25 cc.	20 cc.	1 grm. meal
5a.	None	20 cc.	1 grm. meal
6.	None	20 cc.	0·5 grm. glycinine.

	Cc. N/10 NaOH required after				
No.	24 Hrs.	48 Hrs.	72 Hrs	96 Hrs.	Total.
1.	0·1	0·1	0·1	0·1	0·4
2.	0·3	1·1	0·8	0·7	2·9
3.	2·5	1·5	1·2	1·2	6·4
4.	1·1	1·0	1·0	1·0	4·1
5.	5·5	2·5	—	3·0	11·0
5a.	1·5	1·0	—	4·4	6 9
6.	0·3	0·3	0·3	—	0·9

It is apparent that following the course of lipolysis by means of periodic titrations with alkali is complicated by the acid production of the soy bean in substance and its extracts, both boiled and unboiled. While the acidity developed in Trials 3 and 5 was greater than in the various controls, the very considerable and irregular acid development in the latter is a disturbing feature. The development of acidity by cereal grains is generally recognised, and one of us (J. P. S.) has given some attention to this point in a study of the determination of acidity in cattle feeds (U.S. Dept. of Agr., Bur. of Chem., *Bull.* 122, 160, 1909), but the satisfactory explanation of the phenomenon is not yet presented. That the protein of the soy bean is not the disturbing factor is shown by Trial 6. The most pronounced ester decomposition is exhibited during the first 24-hour interval, some retarding influence being exerted thereafter.

Another experiment was tried, following the suggestion of Reynolds Green ("Soluble Ferments," p. 227). Five grms. of fat-free material were extracted with 100 cc. of 5 per cent NaCl, containing 0·2 per cent KCN, for two hours at 35 to 40°. The preparation was filtered and trials made (1) directly with the filtrate and (2) with the filtrate after "activating" by making slightly acid with dilute acetic acid and allowing to stand two hours longer at 35 to 40°. The unactivated filtrate (1) showed no power to hydrolyse butyrin; the activated filtrate (2) was decidedly active. Twenty cc., equivalent to 1 grm. of soy bean meal, acting upon 0·25 cc. butyrin, required at twenty-four, forty-eight, and seventy-two hour periods 2·0, 1·7, and 2·0 cc., total 5·7 cc. N/10 NaOH to neutralise the acidity developed. The control in which the extract had been boiled required at corresponding intervals 0·6, 0·7, and 1·0 cc, or a total of 2·3 cc. This activated extract also showed lipolysis of an emulsion prepared with soy bean oil. It appears that the spontaneous acid production of the soy bean itself has been largely eliminated by the above process. The amounts of acid developed by the control are uniform and much less than in previous controls, and the decomposition of butyrin is uniform and progressive, not diminishing, as in previous trials.

There is present then a true lipase, which is dissolved by 5 per cent NaCl, and which is either activated by acetic acid or generated by that acid from its zymogen.

Conclusion.

In addition to the urease, amylase, and glucoside-splitting enzyme reported by other workers, the soy bean contains also a protease of the peptoclastic type, a peroxidase, and a lipase. Negative results have been obtained for sucrase and protease of the peptonising type. It was thought unnecessary to examine the material for urease, and no attempt was made to corroborate the presence of the glucoside-splitting enzyme. The presence of an active amylase has been corroborated.

To comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged in Government work will be engaged."

Chemist (40), married, experienced in fine Tar and Wood Products, Acids, High Explosives, and several Synthetic Products seeks Engagement. Can design, put up, and start new Chemical Works. Continental, English, and American experience. Willing to go abroad.—Address, "C 40," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

CHEMISTS.

Wanted at once by a large Controlled Establishment engaged in the supply of War Material of the first importance, a number of Chemists of varied training and experience. Applications, giving full details of training and experience, are invited from Junior Chemists desirous of obtaining experience in analytical work and training in chemical manufactures, from thoroughly trained Research Chemists and from Chemists who have already had experience in manufacture. No one already on Government work need apply.—Apply your nearest Labour Exchange, mentioning this Newspaper and No. A 2154.

UNIVERSITY OF MANCHESTER.

CHEMISTRY COURSES.

Full particulars of the Lecture and Laboratory Courses qualifying for Degrees in Chemistry will be forwarded on application to the Registrar.

Applications for admission to the Research Laboratories should be made to the Director of the Chemical Laboratories.

THE CHEMICAL NEWS
Vol. CXIV., No. 2962.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June or July, as may hereafter be determined.

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A., F. D. Chattaway, M.A., F.R S.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

A new Organic Laboratory has recently been erected and is now in use.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: A. Angel, M.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M A. F.R S *Organic and General Chemistry*, Queen's College Laboratory: F. D. Chattaway, M.A., F.R.S.

Numerous Scholarships, usually of the value of £80 per annum and tenable for four years, are offered every year by the various colleges. They are awarded after a competitive examination in the various branches of Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as a Student of Research, and obtain a degree after two years' residence in the University, by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, Sc.D., F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrators—W. Fearon, B.A., and Edith Wilson, B.A., B Sc.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.

3. *Metallurgy.*—A Course for Engineering and Technical Students.

4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the middle of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

The University also grants the Degree of Bachelor of Science to graduates who have obtained Moderatorship or an Honours Degree equivalent to Moderatorship and have devoted a year to research in the University Laboratory.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(UNIVERSITY OF LONDON).

Professors — Herbert Jackson, F.C.S., &c. (Daniell Professor), and A. W. Crossley, Ph.D., F.R.S., &c.

Assistant Professor—P. H. Kirkaldy, F.I.C., &c.

Lecturers and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., H. W. Cremer, B.Sc., and Herbert Savage.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1916-1917 are Oct. 4, Jan. 17, and May 2.

The general Courses of Lectures on Chemistry deal with the nature and scope of the subject and the principles involved, in relating to one another the experimental facts, shown as illustrations of the properties of the elements and their chief compounds. The non-metallic elements are first treated of, as demonstrating most clearly the characters of the interactions between the different kinds of matter, and as affording the best opportunity of classifying the main groups of compounds met with, when dealing with the inorganic branch of the subject. The metallic elements and their compounds are then discussed, and this part of the Course is completed with a *résumé* in which the connected relations of the properties of the elements are described. The latter portion of the Course embraces in the same manner a study of the principles and properties of the carbon compounds which are examples of the main groups of organic substances. Class Examinations are held from time to time during the Session.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants—S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Tuck, D.Sc.; Irvine Masson, M Sc.; H. Terrey, B.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 2 to December 20; Second Term, from January 16 to March 30; Third Term, from May 1 to July 5.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30. or 3.30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt, ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen fixation; other technical processes, and the properties of metals.

Junior Course of Inorganic Chemistry.

An Introduction to the Principles of Inorganic Chemistry. Special attention will be paid to general points of view, and to the application of physico chemical laws and methods.

First and Second Terms: The Class meets on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays, Fridays, and Saturdays at 9, and Wednesdays at 11.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Senior Course of Physical Chemistry.

Tuesday and Thursday at 9.

A general Course on Physical Chemistry and its applications.

Fee:—Course £5 5s.

General Course of Organic Chemistry.

Monday and Wednesday at 12, Thursday at 3.

Fees:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Monday and Friday at 11. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures and Practical Classes in Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry—W. A. Bone, F.R.S.

Professor of Organic Chemistry—J. F. Thorpe, F.R.S.

Professor of Physical Chemistry—J. C. Philip, M.A., D.Sc.

Assistant Professor—B. Mouat Jones, M.A.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and; subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas are awarded to Students of the several constituent Colleges:—

The Diploma of the Imperial College of Science and Technology (D.I.C.) for advanced study or research in Pure or Applied Science.

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute, (A.C.G.I.) in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their courses. Three Research Fellowships, founded by Mr. Otto Beit. of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of other Universities.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Professors—Chemistry, Henry L. Smith, B.Sc., F.I.C.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean)

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry, Botany, Materia Medica, and Pharmacy commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the Lectures and Practical Work in Chemistry and in Botany are accepted as evidence of scientific training by the Institute of Chemistry in connection with the Examinations for the Associateship. Certificates of attendance at the Lectures and Practical Work in Chemistry are accepted by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy are also accepted by the Conjoint Board, and at the Courses of Pharmacy and Materia Medica by the University of London for the Second Examination for Medical Degrees, Part II.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—Vacant.

Lecture Assistant—(Vacant).

Student Assistant—(Vacant).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 3rd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1916-1917, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, J. O. Hughes, B.Sc., Sybil M. Leslie, M.Sc., Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, M.A., D.Sc., and W. E. Williams, B.Sc.

The Session opens October 3rd, 1916. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s. Physical Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; Composition Fee for all Lectures and Laboratory Classes of the Science Degree Course taken in one year, £16.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constitutent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor of Chemistry—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor of Metallurgy—A. A. Read, D.Met., F.I.C.

Assistant Lecturer and Demonstrator—R. H. Greaves, M.Sc.

The Session commences October 3rd and terminates on June 22nd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 10s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 10s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 15s.

A course on Organic Chemistry will be given in the Session 1917—1918.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £4 per session; eight per week, £6 6s. per session; twelve hours or more per week, £8 8s. per session.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

Students by making a payment of £16 at the commencement of each session may compound for all fees for the whole session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A special prospectus is issued concerning courses of study for diplomas in engineering, mining, and metallurgy.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Department of Chemistry.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., M.B., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electrometallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

Day Lectures.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Three Lectures per week for first Session, two Lectures per week for second Session, and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—*Intermediate Science*—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree* — Three year course after passing the Intermediate Examination (which may be taken on entering the University). The last session is spent on research which is essential for all Honours Degrees in the Faculty of Science. During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.
2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.
3. The Fees for separate Courses of Lectures in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened, for students who have attained the standard of an Inter. B.Sc. examination, from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Second year Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.
2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of Experimental Physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.A., D.Sc., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; Annie M. Herbert, B.Sc.

Demonstrators—H. D. P. Davies and W. J. Gibbs.

Assistant in Chemical Laboratory—H. A. Hobbs.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught in the Faculty of Science of the University of Bristol. The Engineering work of the late University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 25th.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., Sc.D., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators — Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; S. R. Carter, M.Sc.; A. Parker, D.Sc.; J. E. Coates, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 3rd, 1916.

The Chemical Department has hitherto been housed in the new University buildings at Bournbrook, but owing to those buildings having been taken over by the Military Authorities for use as a Base Hospital the classes during the coming Session will be arranged for at the Birmingham Municipal Technical School and the Mason College.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year. — *Advanced Organic Chemistry.*— This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*— This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

The class meets two hours weekly during the Winter and Spring Terms.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry Inorganic, Organic, and Physical) extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9 30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc., F.I C.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—The Principal.
Assistant Professor of Chemistry—B. North, A.R.C.S.
Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; A. Jackson, B.Sc.
Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).
Demonstrator in Physics—F. Harcourt, B.Sc.
Lecturer in Dyeing—M. Fort, M.Sc.
Lecturer in Gas Manufacture—J. W. Roper.
Lecturer in Botany—J. Cryer.
Lecturer in Pharmacy—G. H. Etchells.
Lecturer in Biology—J. A. Fisher.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry and Physics.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. The practical laboratories include a completely equipped Practical Dyehouse and Finishing Rooms.

III. *Chemical Engineering.* Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science.* One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing.* Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board* (*M.R.C.S., L.R.C.P.*), *London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Boards for Medical Studies (London and Dublin) as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor, Major, and Assistants' Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.
Demonstrator—(Killed in War).
Assistant—H. Douglas Elkington, B.Sc., F.I.C.
(Closed during the period of the war).

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.
Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.
Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.
Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc.
Demonstrators—(Three vacant).

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry. — (A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry. — (B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 11 30 a.m. Fee. £4 10s.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 11.30 a.m.; fee, £4 10s. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (*d*) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Praetical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 in the Second and Third Terms Fee, £7 7s.

Colour Chemistry and Dyeing Department.

Professor—A. G. Perkin, F.R.S.. F.I.C.
Lecturer and Research Chemist—J. B. Oesch, Ph.D.
Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.
Demonstrator—A. E. Woodhead, M.Sc.

The Courses extend over periods of (*a*) three or (*b*) four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. Diploma Course (*a*) is suitable for those who purpose to become dyeing chemists, and desire in the future to take part in the direction of the operations of dyeing and calico printing; *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c. Honours Course (*b*) is more largely concerned with the study of colour manufacture, and is designed for the training of factory and research chemists required by works which are engaged in the preparation of dyestuffs.

Textile Industries Department.

Professor—Aldred F. Barker, M.Sc.

Research Lecturer—Howard Priestman.

Research Chemist and Lecturer—W. Harrison, M.Sc.

Research Physicist and Lecturer—S. A. Shorter, D.Sc. (Maintained by the Textile Institute).

The courses of instruction extend over three or four years according to the Degree or Diploma Course selected. Shortened courses are arranged for special sections of the work. The practical equipment is designed to enable workers in the department to pass wool through every process from the Raw Material to the Finished Fabric. The Research Laboratories are equipped for the Scientific Investigation of the fundamental principles underlying all the processes involved in Wool Manufacture. Clothworkers' Scholarships are at the disposal of the University, and it is very probable that under the newly developed West Riding of Yorkshire Scheme valuable Travelling Scholarships will be available for Senior Textile Students.

Leather Industries Department.

Professor—H. R. Procter, D.Sc., F.I.C.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

Demonstrator—F. C. Thompson, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house. In 1914 the capacity of the University to undertake research in this branch of Applied Science was greatly extended by the establishment, in a new building adjoining the Leather Department, of the Procter International Research Laboratory, erected by the leather industries of the world in recognition of the work of Henry Richardson Procter, the first Professor of Leather Industries in the University.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Professor of Agricultural Chemistry—C. Crowther, M.A., Ph.D.

Assistant Lecturers in Agricultural Chemistry—W. Godden, B.Sc., A.R.C.S., F.I.C.; N. M. Comber, B.Sc., A.R.C.S.; J. A. Hanley, Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture at the University Farm.

Institution for Research in Animal Nutrition.

Director—C. Crowther, M.A., Ph.D.

Biochemist—H. W. Dudley, M.Sc., Ph.D.

Research Assistants—H. E. Woodman, M.Sc., Ph.D.; Hilda Woodhouse, M.A., B.Sc.

The Institution is maintained by a special grant from the Board of Agricultute and Fisheries, and is closely associated with the Agricultural Department of the University.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livesey Professor—J. W. Cobb, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. J. Hodsman, M.Sc.

The Courses extend over two, three or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Special attention is paid to the study of Refractory Materials.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, M.Sc., F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Bio-chemistry—W. Ramsden, M.A., D.M.

Professor of Organic Chemistry—R. Robinson, D.Sc.

Lecturer on Metallurgy—Guy D. Bengough, D.Sc., M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—A. J. Allmand, D.Sc.; Francis W. Kay, M.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froysell.

The Session commences October 5th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Associateship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic and Physical Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Course A.—General Elementary Chemistry, £4.
Course B.—Inorganic Chemistry. Fee, £3.
Course C.—Inorganic Chemistry (Honours Course). Fee, £4.
Course D.—Organic Chemistry. Fee, £3.
Course E.—Organic (Honours). Fee, £4.
Course F.—Physical Chemistry. Fee, £3.
Course G.—Honours Physical Chemistry. Fee, £4.
Course H.—Applied Inorganic Chemistry, £2 10s.
Course J.—Metallurgy. Fee, £2 10s.
Course K.—Applied Organic Chemistry. Fee, £2 10s.
Course L.—Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sheridan Muspratt Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1915, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.
(In the University of Durham).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., V.P.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S. (serving with H.M. Forces), and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturers and Demonstrators—A. Foster, M.Sc., Ph.D. (engaged on Munition Work), and J. B. Firth, M.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—A. A. Hall, M.Sc., Ph.D.

First Year Courses—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(*a*) Inorganic Chemistry.—Advanced Course, Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(*b*) Organic Chemistry.—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*c*) Organic Chemistry.—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s per session; £1 10s. per term.

(*d*) History of Chemistry and Chemical Philosophy.—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*e*) Physical Chemistry.—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*f*) Analytical Chemistry. — Fridays at 9.15 a.m. Fee, £1.

(*g*) The Rarer Elements and the Periodic Law.—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the courses *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses, *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects: —(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) Ancient History, (*e*) French, (*f*) German, (*g*) some other language to be approved, (*h*) Experimental Science or Physics or Chemistry, (*i*) Botany or Zoology, (*j*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting there from, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, Sept. 28th, 1916. Candidates should send in their names to the Secretary on or before September 10th.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 9th. Candidates should send in their names to the Secretary on or before September 27th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Organic Chemistry — Arthur Lapworth, D.Sc., F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—*C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; *E. C. Edgar, D.Sc.; F. P. Burt, D.Sc.; J. E. Myers, M.Sc.

Assistant Lecturers and Demonstrators—†W. J. Jones, M.Sc.; †J. R. Partington, M.Sc.; Colin Campbell, M.Sc.; H. Stephen, M.Sc.; W. K. Slater, M.Sc.; Leonora Pearson, M.Sc.

Professor of Metallurgy—C. A. Edwards, D.Sc.

Assistant Lecturer in Metallurgy—W. E. Thornycroft, B.Sc., M.Sc.

Lecturers in Electro-Chemistry—†J. N. Pring, D.Sc.; E. Newbury, D.Sc.

(* Under leave for special work for Ministry of Munitions. † Serving in H.M. Forces).

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays, Wednesdays, and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters — Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Course A, two Lectures per week during the first half of the Session. Course B, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; E. B. R. Prideaux, M.A., D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to

Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturer on Physical Chemistry—W. E. S. Turner, D.Sc., M.Sc.

Lecturers and Demonstrators—W. J. Jarrard, B.Sc.; J. Kenner, D.Sc., Ph.D.; C. R. Young, D.Sc., B.Sc.

Temporary Lecturers and Demonstrators—Emily G. Turner, M.Sc.; Dorothy M. Bennett, M.Sc.; Annie M. Matthews, M.Sc.

The Session will commence October 4th.

Matriculation Course. — Tuesday and Friday at 9.30, Wednesday at 11.30 during Michaelmas and Lent terms. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:— Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:— Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education, Geography.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B. or B.Met.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B Sc. Course in Chemistry.—Monday at 9.30 a.m. and Friday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 p.m., during two terms, Monday at 12.30 p.m. and Thursday at 11.30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s..

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

Lecturer—J. H. Wreaks, B.Met.

Demonstrators—L. Aitchison, D.Met., B.Sc.; F. C. Thompson, B.Sc., D.Met.

Lecturer in Non-ferrous Metallurgy—G. B. Brook.

Demonstrator—F. Orme, B.Met.

Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is dealt with in the Nonferrous Department described below. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and Metallurgical Geology. Practical Metallurgy :—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character. Working accommodation is provided for 30 students at one time. The course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students, provide the means for the Chemical examination of the alloys prepared. A Staff and Post-graduate research laboratory completes the provision for the chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ross microscopes. The recalescence laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Colver-Glauert Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

Degrees are awarded to successful students in Steel Metallurgy, and Associateships in both Steel and Non-ferrous Metallurgy.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph.D., D. ès Sc., F.I.C.

Lecturer—J. W. Dodgson, B.Sc.

Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D., F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for students preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hall, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—Alex. McKenzie, M.A., D.Sc., Ph.D., F.R.S., F.I.C.

Lecturer—J. K. Wood, D.Sc.

Demonstrator—(Vacant).

Lecture Assistant and Lab. Steward—J. Foggie.

The Session consists of three Terms :—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The General Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First M.B., Ch.B.).

The Special and Honours Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Research.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Frederick Soddy, M.A., F.R.S.

Lecturers—Francis W. Gray, M.A., D.Sc.; Joseph Knox, D.Sc.

I. *General Lecture Course, Systematic Chemistry.*—(Daily during the Winter Session at 3 p.m.). These lectures treat of :—(1) The Laws of Chemical Combination and the General Principles of Chemistry, including Chemical Calculations; (2) the Elements classified according to the Periodic Law; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Two written Class Examinations are held. A Tutorial Class (without fee) is held in connection with the General Lecture Course. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s.

II. *Elementary Practical Course for all Students.*—(Spring Term). Demonstration on Monday at 12 noon. For practical work the class will be divided into two groups; one group will meet on Tuesday and Thursday, and the other on Wednesday and Friday, from 10 a.m. to 1 p.m. This course is devoted to practice in Chemical Methods and in Elementary Qualitative Analysis. The instruction is under the direction of the Professor of Chemistry and the Staff. One practical examination is held at the end of the course, namely, the Degree Examination, but it must be attended by all, those not sitting the Degree Examination taking it as a Class Examination. Students in all faculties are required to pass this practical examination as well as the written examination, as part of the requirements for the Degree. The practical course should be taken, whenever possible, concurrently with the Systematic course. Fee, £3 3s. This fee includes the necessary apparatus and appliances, with certain exceptions such as platinum-foil and wire.

Scheme of Lecture Courses for the B.Sc. Degree in Chemistry (subsequent to Courses I. and II.).

III. (*a*) Introductory Physical Chemistry, 15 lectures, by the Professor—Fee, £1 1s., daily at noon for the first three weeks of the Summer Session.

(*b*) Physical Chemistry, 40 lectures—Fee, £2 2s.

(*c*) Inorganic Chemistry, 40 lectures—Fee, £2 2s. (inclusive fee for (*b*) and (*c*) courses, £3 3s.), by Dr. Gray, extending over the last seven weeks of Summer Session (Mon., Wed., Frid., noon), and the following Winter Session (Mon., Tues., Thur., 3—4 p.m. before Christmas, and Mon., Wed., Frid., noon, after Christmas).

(*d*) Advanced Physical Chemistry, 15 lectures, by the Professor—Fee, £1 1s., Thur. and Fri. at noon for the last seven weeks of the Summer Session.

(*e*) Organic Chemistry, 50 lectures, by Dr. Knox—Fee, £3 3s., Winter Session, Mon., Wed., and Fri. at noon before Christmas, and Tues. and Thur. at 3—4 p.m. after Christmas.

IV. *Chemical Laboratory.*—The Laboratory is open daily from 9 a.m. to 5 p.m. Each student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The aim of the Laboratory Courses is to train the student in the practical methods of the science, so as to enable him to conduct chemical analysis and original research, and to apply chemistry to the arts and manufactures. Weekly Demonstrations, attendance on which is compulsory, are held in connection with the Laboratory Courses. (For further information as to fees and other conditions, see "University Fees").

Research.—The Laboratory is open for original work during both the Summer and Winter Sessions.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry and Forest Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.
Assistant—R. Glegg, B.Sc., F.I.C.

I. A Preparatory Course in General Chemistry including Organic Chemistry is given for those who are unable to take the full University Course. The course in Inorganic Chemistry consists of about sixty Lectures with Practical Work (seven hours weekly) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and about thirty hours practical work, and is given during the Summer Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £2 2s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Forest Chemistry* (*General Course*).—Students in Forestry take the greater part of the General Lecture Course in Agricultural Chemistry, with special lectures on the Chemistry of Timber and Forest Products. The early part of the Laboratory Work is the same as in the case of Agricultural Students, but the latter part is occupied with special exercises on Forest Products. Fee, £4 4s.

IV. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry or Forest Chemistry. Fee, £2 2s

V. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or Forest Chemistry, or to undertake research in these subjects.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.
Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; J. E. Mackenzie, Ph.D., D.Sc.; S. A. Kay, D.Sc.; and H. G. Rule, B.Sc., Ph.D., and Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S E.

Staff.—A. Archibald Boon, B.A , D.Sc.; Andrew King, F.I.C.; F. D. Miles, B.Sc.; Clerk Ranken, D.Sc.; James Sandilands, Assoc.H.W.C.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

There is an extensive range of Chemistry Laboratories, embodying the most modern developments in laboratory design and equipment, and including a complete plant for the production of liquid air. The Chemistry Courses are designed to meet the requirements of Analytical and Technical Chemists. The College is a recognised training centre for the examinations of the Institute of Chemistry, and students can obtain the necessary instruction in General Chemistry, and also the specialised instruction required for the Final Examination for the Associateship of the Institute in the departments of Organic Chemistry, Metallurgy, Foods and Drugs, and Bio-chemistry.

The course for the Diploma of the College has been laid down on the same general lines as that required for the examinations of the Institute of Chemistry.

The Chemistry Courses are recognised by the University of Edinburgh as qualifying courses for the B Sc. degree.

Evening Classes are also provided in the subjects of Materia Medica and Botany.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of Technical Mycology of Brewing, Distilling, Yeast Manufacture, Malting, Butter, Margarine, and Cheese Manufacture, Agriculture, Starch, Sugar, Preserve Making, &c. In this laboratory provision is made for the teaching of Biology, and the microscopic examination of Foods and Drugs, in connection with the examinations of the Institute of Chemistry.

Day Classes open on October 10th, and the Evening Classes on September 28th.

Matriculation Fee, 5s.; Composition Fees from £15 15s. to 21 guineas per annum. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D., F.R.S., F.I.C.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens September 26th, 1916.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by attendance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1916-1917 may be had from the Director, Mr. H. F. Stockdale,; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Salvator and St. Leonard.

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

Reader in Organic Chemistry — W. N. Haworth, D.Sc., Ph.D.

The Session begins on October 9th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-six Bursaries, ranging in value from £50 to £10 each per annum, is held annually in June. (For 1917 entries are due May 23rd). One of these is open to Men or Women, and fifteen are restricted to Women, nine of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. The remainder are open to men only.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree. and the M.B., Ch.B. Degrees.; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. K. Macbeth, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—*Advanced Chemistry.*—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—*Practical Chemistry for Engineering Students.*—A special course is given during the first term. Fee, £3 3s.

V.—*Laboratory Pupils.*—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m.—5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £73 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years, and also one of the Industrial Bursaries.

UNIVERSITY COLLEGE, CORK.

A Constituent College of the National University of Ireland.

Professor—Augustus Edward Dixon, M.D.

Assistant Lecturer—John Taylor, M.Sc.

Demonstrator—H. R. S. Clotworthy, B.Sc.

The College Session will commence in October, 1916, and end in June, 1917. All classes are open to male and to female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Miss R. Clarke, B.A., D.Sc., and Denis Madden, A.R.C.Sc.I., A.I.C.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical hormathic and cyclic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, but not including organic chemistry.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the final practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students :—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are six Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for three years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Entrance Scholarships and Teacherships-in-Training in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION

(F.I.C. AND A.I.C.).

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to maintain the efficiency and integrity of the profession of Chemistry, including professional consulting and technological chemists, public analysts, and chemical advisers. *The Studentship.*—Every Candidate for registration as a Student is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate Examination. A Candidate who has passed the Intermediate Examination of the Institute, or has been exempted therefrom, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associateship* (*A.I.C.*).—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship* (*F.I.C.*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Russell Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute—The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. Technological Examinations are conducted once every year at various centres throughout the kingdom. Programmes of the respective Colleges may be had on application. *City and Guilds* (*Engineering*) *College, Exhibition Road.*—The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting.

CITY OF LONDON COLLEGE, White Street, Moorfields.—A. W. Bain, B A., B.Sc., F.I.C., and Assistants. Classes and Laboratory Practice in Chemistry, Botany, and Geology, open to Students of both sexes. Courses on Commercial Products—Milling (Flour), Tea, Textiles Session commences Sept. 25.

THE POLYTECHNIC, Regent Street, W.—Frank E. Weston, B.Sc., F.C.S., and Assistants General, Technical, and Applied Chemistry. Gas Manufacture and Analysis, Paints and Varnishes, Oils and Fats, Dairy Products, Conjoint Board Chemistry (Dental and Medical), Course for Lady Dispensers. Special research laboratory. Session commences Sept. 27.

BATTERSEA POLYTECHNIC.—Principal, F. H. Newman, M.A., Ph.D. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Complete three or four years' diploma courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Mathematics, Chemical Engineering and Engineering subjects, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examinations (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses (theoretical and practical) in various Technical subjects, as Chemical Engineering, Fuel, Coal-tar Colours, Applied Bacteriology, Food and Drug Analysis, Pharmacy and Dispensing, Materia Medica, Paper Making and Testing, Oils and Fats, Toilet Soap Manufacture, Lubricating Oils, Dyeing and Cleaning. Special day and evening courses for the examination of the Institute of Chemistry, the Pharmaceutical Society, the Apothecaries' Hall, and the Conjoint Medical Board. For further information see the Polytechnic Calendar, an abridged copy of which may be obtained gratis from the Secretary of the Polytechnic.

BOROUGH POLYTECHNIC INSTITUTE, Borough Road S.E.—Chemistry Department under the Direction of C. Dorée, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see Institute Syllabus).

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by G. Senter, D.Sc., Ph.D. (assisted by G. W. Clough, D.Sc., F. Barrow, M.Sc., G. Martin, D Sc., Maude O. Newling, B.Sc., Gwladys M. Lander, and A. Norah Kershaw), prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 25. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

NORTHERN POLYTECHNIC INSTITUTE, Holloway, London, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. Prospectus sent free on application to the Secretary.

NORTHAMPTON POLYTECHNIC INSTITUTE, St. John Street, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Day Courses in Electro-chemistry and Engineering Chemistry, and evening classes in Electro-chemistry, Electro-plating, Engineering Chemistry, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus). Telephone, Holborn 1194.

SOUTH WESTERN POLYTECHNIC INSTITUTE, Manresa Road, Chelsea. — This Institute offers facilities for academic and technical education in many branches of Chemistry and Metallurgy. The department has designed both day and evening courses to meet the many requirements of these professions in London. Complete courses in General Chemistry, Metallurgy, and Assaying requisite for the B.Sc. and A.I.C. Examinations, Technical Courses. Ample opportunity for individual work has been arranged for both day and evening students. A full list of these courses will be supplied on application. A feature of the laboratory work is the facility given for specialising in any particular branch of the above subjects, thus supplying a much needed want to men who have neither the time nor necessity for attending a degree course. The various lecturers will be pleased to advise intending students with regard to selection of courses. The department is under the control of J. B. Coleman, A.R.C.S., F.I.C., F.C.S., and the aim of the Institute is to make its courses of sound practical use to those engaged in Chemical Industries. Further particulars respecting the courses can be obtained from the Secretary (Room 79).

EAST LONDON COLLEGE, Mile End Road.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R S Willows, M.A., D.Sc., H. J. S. Sand, D.Sc., Ph.D., G. F. Morrell, B.Sc., Ph D., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., M.I.M.M., G. Patchin, A.R.S.M., E M Boote, Assoc.Inst.C.E., Arthur Harden, D.Sc., F R S., &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Harlow, B Sc., &c. The new Session of the Sir John Cass Technical Institute, which is especially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, September 25th. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction and on inorganic, organic, physical, and analytical chemistry, which form a special feature of the work of the Institute. The curriculum in connection with the Fermentation Industries includes courses of instruction on Brewing and Malting, and on the Microbiology of the Fermentation Industries. In the department of Physics and Mathematics, a special course of Lectures will be given on the Methods of Differential and Integral Calculus and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application of modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses, special advanced courses are provided on Gold, silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Heat Treatment of Iron and Steel, and on the Mechanical Testing of Metals and Alloys. Full facilities for advanced practical work and research in Chemistry, Metallurgy, and Physics.

EAST HAM TECHNICAL COLLEGE.—Principal, W. H. Barker, B.Sc. Head of Chemical Department—A. E.

Dunstan, D.Sc. (Lond.). Lecturers—F. B. Thole, D.Sc.; E. D. Griffiths, B.Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaice; A. G. Mussell. Chemical Engineering and Gas Engineering—A. J. Nice. Gas Supply—G. Jenkins. Soap Manufacture—C. J. Benedict. Oils, Fats, and Waxes—J. H. Baxter. Tar Distillation, &c.—A. J. Nice and A. E. Dunstan, D Sc. Metallurgy—F. B Thole, D.Sc. Sugar Manufacture—A. Wade. Painters' Oils, Colours, and Varnishes—R. A. Phillips. Evening Classes and Secondary School.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Robert H. Pickard, D.Sc.(Lond.)., &c., assisted by Jos. Yates, M.Sc., F.I.C., L. Letter. M.Sc., and Hannah de Pennington, B.Sc. Session commences Sept. 25. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

REDRUTH SCHOOL OF MINES (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the School Mine. Syllabus on application.

MANCHESTER SCHOOL OF TECHNOLOGY (University of Manchester.—The work of the School of Technology includes advanced study and research in various branches of science and technology, and undergraduate courses in the Faculty of Technology, extending over three years and leading to Degrees and Certificates in Mechanical Engineering, Electrical Engineering, Sanitary Engineering, Textile Industries, Printing and Photographic Technology, Architecture, and in the following branches of Applied Chemistry:—General Chemical Technology, Chemistry of Textiles (Bleaching, Dyeing, Printing, and Finishing), Paper Manufacture, Metallurgy and Assaying, Fuels, Chemical Technology of Brewing, Electro-chemistry, Photography. The provision for the teaching of Chemistry is of an exceptionally complete character. In addition to the laboratories for Inorganic and Organic Chemistry, Metallurgy, Brewing, Bleaching, Dyeing, and Electro-chemistry, an extensive equipment (including machinery and appliances on an industrial scale) for demonstration, experiment, and original research in connection with the Bleaching, Dyeing, Printing, and Finishing, and Papermaking industries is provided in a separate building. A Brewhouse is also equipped on the low gravity principle with a plant of four bushel capacity.

TECHNICAL COLLEGE, SWANSEA.—Principal, W. M. Varley, M.A., D.Sc., Ph D. Chemistry, E. A. Tyler, M.A.; Metallurgy, H. I. Coe, M.Sc.; Physics, J. C. Kirkman, B.Sc.; Secretary, W. James. Day and Evening Courses in Pure and Applied Chemistry, Chemical Engineering, Metallurgy, and for Pharmaceutical, Medical, and Dental Students. Session opens Sept. 18th.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Principal, J D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D., and W. J. Lewis, B.Sc.; Physics, A. T. Harrison, B Sc.; Botany, Miss O. E. Ashdown, B.Sc. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Sept. 11th. For other particulars and programme, apply G. F. Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, F.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph D., D.Sc. Day and Evening Courses.

NOTICES OF BOOKS.

The Emission of Electricity from Hot Bodies. By O. W. RICHARDSON, F.R.S., Wheatstone Professor of Physics, King's College, London. London: Longmans, Green, and Co. Price 9s.

THE above work forms another contribution to the series of monographs on Physics edited by Sir J. J. Thomson, O.M., F.R.S., and Frank Horton, Sc.D. The subject is exhaustively presented, and in addition to a great mass of original notes from the author's own researches, recent observations and data from all sources are included, very full references being given in each case; the authors quoted number no less than 160.

Systematic investigation of the emission of electrons from hot bodies is a comparatively new subject; isolated observations have been made during the past thirty years in many directions that have not been easy to interpret. The classical investigations of Sir J. J. Thomson and others, resulting in the discovery of the electron and its movements, has enabled research to be conducted upon the sound foundation of established laws.

Prof. Richardson is well known by the volume of his work in this direction. He states in his preface that it was undesirable to include in the book an account of the numerous and important technical developments of the subject; to have done this with any approach to completeness would have been practically impossible in the compass of one volume. The book occupies some 300 pages, and is well indexed and illustrated.

A general introductory chapter is first given containing illustrated descriptions of the experimental methods of working as practised in the author's laboratory; in this section is found a useful table of "fixed temperatures," compiled from various sources, ranging from liquid hydrogen at −253° C. to the melting-point of tungsten at 3276° C.

In the chapters that follow the phenomena of the emission of electron under all known conditions are presented and discussed in a manner that is only possible when the author is thoroughly conversant with the full detail of the subject.

As has already been noted no attempt has been made to enumerate the many technical applications of electron emission; among the more important are the various instruments for rectifying alternating currents, and the production of X-rays by pure electron discharge as in the recently introduced Coolidge X-ray tube, and applications are multiplying rapidly. The editors and publishers are to be congratulated upon having overcome the difficulties connected with the issue of the work at the present time, and in the near future, when a large amount of the energy now occupied in other directions will be available for research and production, the monograph will be found of the greatest value.

Chemistry in the Service of Man. By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C. London, New York, Bombay, Calcutta, Madras: Longmans, Green, and Co. 1916. Pp. x.+255. Price 5s. net.

THE basis of this work was the series of Thomson Lectures delivered by the author before the United Free Church College, Aberdeen, at the end of 1915. In these lectures an attempt was made (and made with great success) to give the general public an insight into the nature and magnitude of the civilised world's debt to the chemist, and the book cannot fail to stimulate and feed the slowly awakening interest in scientific work which is appearing in England. Books of this type are precisely what is wanted in our language. Well written, in a literary style which is above reproach, with an unimpeachable knowledge of the subjects discussed, Dr. Findlay's work gives a temperate and yet enthusiastic review of the material benefits of the application of chemical theories and knowledge, while at the same time the cultural and ethical value of the study of science is clearly kept in view. The introductory first chapter gives a short historical account of the development of modern chemical theory, and then combustion, illuminants, fuels, and explosives are discussed in succession. Later chapters deal, among other subjects, with cellulose and cellulose products, the fixation of atmospheric nitrogen, glass, soda, soap, the colloidal state, synthetic chemistry. The names of the great pioneers are linked with the account of each development of the science, and the book provides a really fascinating narrative of the progress of chemical knowledge.

Discovery or The Spirit and Service of Science. By R. A. Gregory. London: Macmillan and Co., Ltd. 1916. Pp. viii. + 340. Price 5s. net.

It is difficult to restrain over-enthusiasm in writing a notice of this book. Time-worn epithets of praise, recommendations to purchase and read, would possibly give a false idea of its significance. Prof. Gregory has a real message for the world and a real gift in proclaiming it, and his book has appeared at a moment when the people appear to be ready to hear, to be convinced, and to act. Writing with a very wide knowledge of science, a keen interest in literary achievements, and a firm conviction that there should be no antipathy between scientific and humanistic studies, Prof. Gregory's text may be taken from his preface: "Science is not to be measured by practical service alone, though it may contribute to material prosperity; it is an intellectual outlook, a standard of truth, and a gospel of light." He shows how the instinct for truth is man's most priceless possession, and how upon it must be founded all scientific work worthy of the name. The attitude of the great masters and pioneers of science towards the truth is described and illustrated by many excellently chosen quotations, and the biographical notes and anecdotes of eminent scientific men make the book entertaining and pleasant to read. The chapter on Belief and Evidence contains interesting discussions of many fallacious notions and popular superstitions, and Inquiry and Interpretation, and Law and Principle are equally lucidly treated. Perhaps the most convincing chapter is that on the Conquest of Disease, in which the work of Jenner, Pasteur, Simpson, and others is admirably described, while the utilitarian (and possibly the term may be taken to include the majority of young students, as well as adults of the "practical man" type), who is incapable of realising the value of investigations pursued for the sake of acquiring new knowledge without reference to the value of its applications, will get a good deal of enlightenment from the chapter on Practical Purpose, while hardly anybody's imagination could fail to be inspired and stimulated by the last chapters—Across the Border and Towards Infinity. It would be no bad thing for the nation if every child of fifteen or more in every school in the kingdom, and if every grown person, whose mind, however steeped in literary or classical subjects, had not utterly lost the receptivity of youth, could be persuaded to read carefully and thoroughly assimilate Prof. Gregory's book (and probably very little persuasion would be needed in the case of the average boy or girl). It is not easy to summarise its value in a few words nor adequately to describe its merits. The reader would get from it a good deal of knowledge of the fundamentals of all the sciences—and even specialists in one branch are often astonishingly ignorant of the principles of another. In addition he would learn something of the lives of the great men of science, their methods of attacking problems, their most notable achievements. He would have graphically put before him the steps by which scientific knowledge has been applied for the benefit of the human race and civilisation has progressed. But possibly the chief interest of the book lies in the author's insistence upon the educative and ethical value of the study of natural science. Industriousness, patience, accuracy, self-sacrifice, impartiality, and, above all, a passion for truth at all costs, are the ideals which are put before the child in its study of the sciences, and what aims are higher or what lessons are more necessary for us to take to heart?

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 24, June 13, 1916.

Synthesis of Ammonia.—M. Zenghelis.—The author has studied the synthesis of ammonia at the ordinary or a rather higher temperature from nitrogen and hydrogen in the atomic state (nascent state or occlusion of hydrogen by metals). Platinum, palladium, colloidal silver, &c., were employed as catalysts. Only small quantities of ammonia were obtained when either the one or other element was in the atomic state, but the yields were very considerably greater when they were both in the atomic state. The most powerful catalyst was colloidal palladium.

MISCELLANEOUS.

Association of British Chemical Manufacturers.—The Council of this newly-constituted Association has appointed as General Secretary Sir Charles H. Bedford, LL.D., D.Sc. The business of the Association is temporarily being carried on at the Offices of the Society of Chemical Industry, Broadway Chambers, Westminster, S.W.

Iron and Steel Institute.—Autumn Meeting, 1916.—The Autumn Meeting of the Institute will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, September 21 and 22, 1916, commencing at 10.30 a.m. on the 21st and at 10 a.m. on the 22nd. The following is the programme of proceedings:—

Thursday, September 21 (*at* 10.30 *a.m.*).

General Meeting of Members.

Scrutineers will be appointed for the examination of voting papers for election of new Members of the Institute.

A selection of papers will be read and discussed (Nos. 6, 1, 4).

The Council will give notice of amendment of by-laws

Friday, September 22 (*at* 10 *a.m.*).

General Meeting of Members.

A selection of papers will be read and discussed (Nos. 3, 7, 5).

The following is the list of papers that are expected to be submitted for reading and discussion:—

1. H. Brearley—"Some Properties of Ingots."
2. Prof. E. D. Campbell—"Influence of Heat-Treatment on the Thermo-Electric Properties and Specific Resistance of Carbon Steels."
3. Dr. H. M. Howe and A. G. Levy—"Heat Treatment of Eutectoid Carbon Steels."
4. J. N. Kilby—"Steel Ingot Defects."
5. Herbert K. Scott—"Manganese Ores of the Bukowina, Austria."
6. Dr. J. E. Stead, F.R.S.—"Influence of Elements on the Properties of Steel."
7. Dr. J. E. Stead, F.R.S.—"Notes on (*a*) Nickel Steel Scale. (*b*) On the Reduction of Solid Nickel and Copper Oxides by Solid Iron. (*c*) On Effect of Blast Furnace Gases on Wrought Iron."
8. G. F. Zimmer—"Use of Meteoric Iron by Primitive Man."

THE CHEMICAL NEWS

Vol. CXIV., No. 2963.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Newcastle-on-Tyne, 1916.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Arthur Evans, D.Litt., LL.D., P.S.A., F.R.S.,
Extraordinary Professor of Prehistoric Archæology, Oxford; Correspondent de l'Institut de France, &c.

New Archæological Lights on the Origins of Civilisation in Europe: its Magdalenian Forerunners in the South-West and Ægean Cradle.

Et quasi cursores vitaï lampada tradunt.

When I was asked on behalf of the Council of the British Association to occupy the responsible post of President at the Meeting in this great city—the third that has taken place here—I was certainly taken by surprise, the more so as my own subject of research seemed somewhat removed from what may be described as the central interests of your body. The turn of archæology, however, I was told, had come round again on the rota of the sciences represented, nor could I be indifferent to the fact that the last Presidential Address on this theme had deen delivered by my father at the Toronto Meeting of 1897.

Still, it was not till after considerable hesitation that I accepted the honour. Engaged as I have been through a series of years in the work of excavation in Crete—a work which involved not only the quarrying but the building up of wholly new materials, and has entailed the endeavour to classify the successive phases of a long, continuous story, absorbed and fascinated by my own investigations, I am oppressed with the consciousness of having been less able to keep pace with the progress of fellow explorers in other departments or to do sufficient justice to their results. I will not dwell, indeed, on those disabilities that result to myself from present calls and the grave preoccupations of the hour, that to a greater or less extent must affect us all.

But archæology—the research of ancient civilisations—when the very foundations of our own are threatened by the New Barbarism! The investigation of the ruins of the past, at a time when hell seems to have been let loose to strew our continent with havoc beyond the dreams of Attila! "The science of the spade," at a moment when that science confronts us at every hour with another and a sterner significance! The very suggestion of such a subject of discourse might seem replete with cruel irony.

And yet, especially as regards the prehistoric side of archæology, something may be said for a theme which in the midst of Armageddon draws our minds from present anxieties to that still, passionlesss domain of the Past which lies behind the limits even of historic controversies. The science of antiquity, as there seen in its purest form, depends indeed on evidence and rests on principles indistinguishable from those of the sister science of geology. Its methods are stratigraphic. As in that case, the successive deposits and their characteristic contents, often of the most fragmentary kind, enable the geologist to reconstruct the fauna and flora, the climate and physical conditions, of the past ages of the world and to follow out their gradual transitions or dislocations, so it is with the archæologist in dealing with unwritten history.

In recent years—not to speak of the revelations of Late Quaternary culture, on which I shall presently have occasion to dwell—in Egypt, in Babylonia, in Ancient Persia, in the Central Asian deserts, or, coming nearer home, in the Ægean lands, the patient exploration of early sites, in many cases of huge stratified mounds, the unearthing of buried buildings, the opening of tombs, and the research of minor relics, has reconstituted the successive stages of whole fabrics of former civilisation, the very existence of which was formerly unsuspected. Even in later periods archæology as a dispassionate witness has been continually checking, supplementing, and illustrating written history. It has called back to our upper air, as with a magician's wand, shapes and conditions that seemed to have been irrevocably lost in the night of Time.

Thus evoked, moreover, the Past is often seen to hold a mirror to the Future, correcting wrong impressions—the result of some temporary revolution in the whirligig of Time—by the more permanent standard of abiding conditions, and affording in the solid evidence of past well-being the "substance of things hoped for." Nowhere indeed has this been more in evidence than in that vexed region between the Danube and the Adriatic, to-day the home of the Serbian race, to the antiquarian exploration of which many of the earlier years of my own life were devoted.

What visions, indeed, do those investigations not recall! Imperial cities, once the seats of wide administration and of prolific mints, sunk to neglected villages, vestiges of great engineering works, bridges, aqueducts, or here a main line of ancient highway hardly traceable even as a track across the wilderness! Or, again, the signs of mediæval revival above the Roman ruins, remains of once-populous mining centres scattered along the lone hill-side; the shells of stately churches with the effigies, bullet-starred now, of royal founders, once champions of Christendom against the Paynim—nay, the actual relics of great rulers, law-givers, national heroes, still secreted in half-ruined monastic retreats!

Sunt lacrimæ rerum et mentem mortalia tangunt:

Even the archæologist incurs more human debts, and the evocation of the Past carries with it living responsibilities!

It will be found, moreover, that such investigations have at times a very practical bearing on future developments. In connection with the traces of Roman occupation I have recently, indeed, had occasion to point out ("The Adriatic Slavs and the Overland Route to Constantinople," *Geographical Journal*, 1916, 241 *seqq*) that the section of the great Roman road that connected the valleys of the Po and Save across the lowest pass of the Julians, and formed part of the main avenue of communication between the Western and the Eastern provinces of the Empire, has only to be restored in railway shape to link together a system of not less value to ourselves and our allies, for we should thus secure, via the Simplon and Northern Italy, a new and shorter Overland Route to the East, in friendly occupation throughout, which is to-day diverted by unnatural conditions past Vienna and Budapest. At a time when Europe is parcelled out by less cosmopolitan interests the evidence of Antiquity here restores the true geographical perspective.

Whole provinces of ancient history would lie beyond our ken—often through the mere loss of the works of classical authors—were it not for the results of archæological research. At other times again it has redressed the balance where certain aspects of the ancient world have been brought into unequal prominence, it may be, by mere accidents of literary style. Even if we take the Greek World, generally so rich in its literary sources, how comparatively little should we know of its brilliant civilisation, as illustrated by the great civic foundations of Magna Graecia and Sicily, if we had to depend on its written sources alone. But the noble monuments of those regions, the results of excavation, the magnificent coinage—a sum of evidence illustrative in turn of public and private life, of art and religion, of politics and of economic conditions—have gone far to supply the lacuna, Look, too, at the history of the Roman Empire. How defective and misleading in many departments are the literary records! It has been by methodical researches into evidence such as the above, notably in the epigraphic field, that the most trustworthy results have been worked out.

Take the case of Roman Britain. Had the lost books of Ammianus relating to Britain been preserved we might have had in his rugged style some partial sketch of the Province as it existed in the age of its most complete Romanisation. As it is, so far as historians are concerned, we are left in almost complete darkness. Here, again, it is through archæological research that light has penetrated, and, thanks to the thoroughness and persistence of our own investigators, town sites such as Silchester in Roman Britain have been more completely uncovered than those of any other province (see Haverfield, "Roman Britain in 1913," p. 86). Nor has any part of Britain supplied more important contributions in this field than the region of the Roman Wall, that great limitary work between the Solway and the mouth of the Tyne that once marked the northernmost European barrier of civilised dominion.

Speaking here, on the site of Hadrian's bridge-head station, that formed its eastern key, it would be impossible for me not to pay a passing tribute, however inadequate, to the continuous work of exploration and research carried out by the Society of Antiquaries of Newcastle, now for over a hundred years in existence, worthily seconded by its sister Society on the Cumbrian side, and of which the volumes of the respective *Proceedings* and *Transactions*, *Archæologia Æliana*, and last but not least the *Lapidarium Septentrionale*, are abiding records. The basis of methodical study was here the Survey of the Wall carried out, together with that of its main military approach, the Watling Street, by MacLauchlan, under the auspices of Algernon, fourth Duke of Northumberland. And who, however lightly touching on such a theme, can overlook the services of the late Dr. Collingwood Bruce, the Grand Old Man not only of the Wall itself but of all pertaining to Border antiquities, distinguished as an investigator for his scholarship and learning, whose lifelong devotion to his subject and contagious enthusiasm made the Roman Wall, as it had never been before, a household word?

New points of view have arisen, a stricter method and a greater subdivision of labour have become imperative in this as in other departments of research. We must therefore rejoice that local explorers have more and more availed themselves of the co-operation and welcomed the guidance of those equipped with comparative knowledge drawn from other spheres. The British Vallum, it is now realised, must be looked at with perpetual reference to other frontier lines, such as the Germanic or the Rhætian *limes*; local remains of every kind have to be correlated with similar discoveries throughout the length and breadth of the Roman Empire.

This attitude in the investigation of the remains of Roman Britain, the promotion of which owes so much to the energy and experience of Prof. Haverfield, has in recent years conducted excavation to specially valuable results. The work at Corbridge, the ancient Corstopitum, begun in 1906 and continued down to the autumn of 1914, has already uncovered throughout a great part of its area the largest urban centre—civil as well as military in character—on the line of the Wall, and the principal store-base of its stations. Here, together with well-built granaries, workshops, and barracks, and such records of civic life as are supplied by sculptured stones and inscriptions, and the double discovery of hoards of gold coins, has come to light a spacious and massively constructed stone building, apparently a military storehouse, worthy to rank beside the bridge-piers of the North Tyne, among the most imposing monuments of Roman Britain. There is much here, indeed, to carry our thoughts far beyond our insular limits. On this, as on many other sites along the Wall, the inscriptions and reliefs take us very far afield. We mark the gravestone of a man of Palmyra, an altar of the Tyrian Hercules—its Phœnician Baal—a dedication to a pantheistic goddess of Syrian religion, and the rayed effigy of the Persian Mithra. So, too, in the neighbourhood of Newcastle itself, as elsewhere on the Wall, there was found an altar of Jupiter Dolichenus, the old Anatolian God of the Double Axe, the male form of the divinity once worshipped in the prehistoric Labyrinth of Crete. Nowhere are we more struck than in this remote extremity of the Empire with the heterogeneous religious elements, often drawn from its far Eastern borders, that before the days of the final advent of Christianity Roman dominion had been instrumental in diffusing. The Orontes may be said to have flowed into the Tyne as well as the Tiber.

I have no pretension to follow up the various affluents merged in the later course of Greco-Roman civilisation, as illustrated by these and similar discoveries throughout the Roman World. My own recent researches have been particularly concerned with the much more ancient cultural stage—that of prehistoric Crete—which leads up to the Greco-Roman, and which might seem to present the problem of origins at any rate in a less complex shape. The marvellous Minoan civilisation that has there come to light shows that Crete of four thousand years ago must unquestionably be regarded as the birth-place of our European civilisation in its higher form.

But are we, even then, appreciably nearer to the fountain-head?

A new and far more remote vista has opened out in recent years, and it is not too much to say that a wholly new standpoint has been gained from which to survey the early history of the human race. The investigations of a brilliant band of prehistoric archæologists, with the aid of representatives of the sister sciences of Geology and Palæontology, have brought together such a mass of striking materials as to place the evolution of human art and appliances in the last Quaternary Period on a far higher level than had even been suspected previously. Following in the footsteps of Lartet, and after him Rivière and Piette, Professors Cartailhac, Capitan, and Boule, the Abbé Breuil, Dr. Obermeier, and their fellow investigators have revolutionised our knowledge of a phase of human culture which goes so far back beyond the limits of any continuous story, that it may well be said to belong to an older World.

To the engraved and sculptured works of Man in the "Reindeer Period" we have now to add not only such new specialities as are exemplified by the moulded clay figures of life-size bisons in the Tuc d'Audoubert Cave, or the similar high reliefs of a procession of six horses cut on the overhanging limestone brow of Cap Blanc, but whole galleries of painted designs on the walls of caverns and rock shelters.

So astonishing was this last discovery, made first by the Spanish investigator, Señor de Sautuola—or rather his little daughter—as long ago as 1878, that it was not till after it had been corroborated by repeated finds on the French side of the Pyrenees—not, indeed, till the beginning of the present century—that the Palæolithic Age of these rock paintings was generally recognised. In their most developed stage, as illustrated by the bulk of the figures in the Cave of Altamira itself, and in those of Marsoulas in the Haute Garonne, and of Font de Gaume in the Dordogne, these primeval frescoes display not only a consummate mastery of natural design but an extraordinary technical resource. Apart from the charcoal used in certain outlines, the chief colouring matter was red and yellow ochre, mortars and palettes for the preparation of which have come to light. In single animals the tints are varied from black to dark and ruddy brown or brilliant orange, and so, by fine gradations, to paler nuances, obtained by scraping and washing. Outlines and details are brought out by white incised lines, and the artists availed themselves with great skill of the reliefs afforded by convexities of the rock surface. But the greatest marvel of all is that such polychrome masterpieces as the bisons, standing and couchant, or with limbs huddled together, of the Altamira Cave, were executed on the ceilings of inner vaults and galleries where the light of day has never penetrated. Nowhere is there any trace of smoke, and it is clear that great progress in the art of artificial illumination had already been made. We now know that stone lamps, decorated in one case with the engraved head of an ibex, were already in existence.

Such was the level of artistic attainment in South-Western Europe, at a modest estimate some ten thousand years earlier than the most ancient monuments of Egypt or Chaldæa! Nor is this an isolated phenomenon. One by one, characteristics, both spiritual and material, that had been formerly thought to be the special marks of later ages of mankind have been shown to go back to that earlier World. I myself can never forget the impression produced on me as a privileged spectator of a freshly uncovered interment in one of the Balzi Rossi Caves—an impression subsequently confirmed by other experiences of similar discoveries in these caves, which together first supplied the concordant testimony of an elaborate cult of the dead on the part of Aurignacian Man. Tall skeletons of the highly-developed Cro-Magnon type lay beside or above their hearths, and protected by great stones from roving beasts. Flint knives and bone javelins had been placed within reach of their hands, chaplets and necklaces of sea-shells, fish-vertebræ, and studs of carved bone had decked their persons. With these had been set lumps of iron peroxide, the red stains of which appeared on skulls and bones, so that they might make a fitting show in the Under-world.

> "Colours, too, to paint his body,
> Place within his hand,
> That he glisten, bright and ruddy,
> In the Spirit Land!"
>
> Schiller, *Nadowessier's Todtenlied.*

Nor is it only in this cult of the departed that we trace the dawn of religious practices in that older World. At Cogul we may now survey the ritual dance of nine skirted women round a male Satyr-like figure of short stature, while at Alpera a gowned sister ministrant holds up what has all the appearance of being a small idol. It can hardly be doubted that the small female images of ivory, steatite, and crystalline talc from the same Aurignacian stratum as that of the Balzi Rossi internments, in which great prominence is given to the organs of maternity, had some fetichistic intention. So, too, many of the figures of animals engraved and painted on the inmost vaults of the caves may well have been due, as M. Salomon Reinach has suggested, to the magical ideas prompted by the desire to obtain a hold on the quarries of the chase that supplied the means of livelihood.

In a similar religious connexion may be taken the growth of a whole family of signs, in some cases obviously derivatives of fuller pictorial originals, but not infrequently simplified to such a degree that they resemble or actually reproduce letters of the alphabet. Often they occur in groups like regular inscriptions, and it is not surprising that in some quarters they should have been regarded as evidence that the art of writing had already been evolved by the men of the Reindeer Age. A symbolic value certainly is to be attributed to these signs, and it must at least be admitted that by the close of the late Quaternary Age considerable advance had been made in hieroglyphic expression.

The evidences of more or less continuous civilised development reaching its apogee about the close of the Magdalenian Period have been constantly emerging from recent discoveries. The recurring "tectiform" sign had already clearly pointed to the existence of huts or wigwams; the "scutiform" and other types record appliances yet to be elucidated, and another sign well illustrated on a bone pendant from the Cave of St. Marcel has an unmistakable resemblance to a sledge. (This interpretation suggested by me after inspecting the object in 1902 has been approved by the Abbé Breuil, *Anthropologie*, xiii., p. 152, and by Professor Sollas, "Ancient Hunters," 1915, p. 480). But the most astonishing revelation of the cultural level already reached by primeval man has been supplied by the more recently discovered rock paintings of Spain. The area of discovery has now been extended there from the Province of Santander, where Altamira itself is situated, to the Valley of the Ebro, the Central Sierras, and to the extreme South-Eastern region, including the Provinces of Albacete, Murcia, and Almeria, and even to within the borders of Granada.

One after another, features that had been reckoned as the exclusive property of Neolithic or later Ages are thus seen to have been shared by Palæolithic Man in the final stage of his evolution. For the first time, moreover, we find the productions of his art rich in human subjects. At Cogul the sacral dance is performed by women clad from the waist downwards in well-cut gowns, while in a rock-shelter of Alpera (that of Carasoles del Bosque; Breuil, *Anthropologie*, 1915, xxvi., p. 329 *seqq.*), where we meet with the same skirted ladies, their dress is supplemented by flying sashes. On the rock painting of the Cueva de la Vieja, near the same place, women are seen with still longer gowns rising to their bosoms. We are already a long way from Eve!

It is this great Alpera fresco which, among all those discovered, has afforded most new elements. Here are depicted whole scenes of the chase in which bow-men—up to the time of these last discoveries unknown among Palæolithic representations—take a leading part, though they had not as yet the use of quivers. Some are dancing in the attitude of the Australian Corroborees. Several wear plumed head-dresses, and the attitudes at times are extraordinarily animated. What is specially remarkable is that some of the groups of these Spanish rock paintings show dogs or jackals accompanying the hunters, so that the process of domesticating animals had already begun. Hafted axes are depicted as well as cunningly-shaped throwing sticks. In one case at least we see two opposed bands of archers—marking at any rate a stage in social development in which organised warfare was possible—the beginnings, it is to be feared, of "kultur" as well as of culture!

Nor can there be any question as to the age of these scenes and figures, by themselves so suggestive of a much later phase of human history. They are inseparable from other elements of the same group, the animal and symbolic representations of which are shared by the contemporary school of rock-painting north of the Pyrenees. Some are overlaid by palimpsests, themselves of Palæolithic character. Among the animals actually depicted, moreover, the elk and bison distinctly belong to the Late Quaternary fauna of both regions, and are unknown there to the Neolithic deposits.

In its broader aspects this field of human culture, to which, on the European side, the name of Reindeer Age may still, on the whole, be applied, is now seen to have been very widespread. In Europe itself it permeates a large area—defined by the boundaries of glaciation—from Poland, and even a large Russian tract, to Bohemia, the upper course of the Danube and of the Rhine, to South-Western Britain and South-Eastern Spain. Beyond the Mediterranean, moreover, it fits on under varying conditions to a parallel form of culture, the remains of which are by no means confined to the Cis-Saharan zone, where incised figures occur of animals like the long-horned buffalo (*Bubalus antiquus*) and others long extinct in that region. This Southern branch may eventually be found to have a large extension. The nearest parallels to the finer class of rock-carvings as seen in the Dordogne are, in fact, to be found among the more ancient specimens of similar work in South Africa, while the rock-paintings of Spain find their best analogies among the Bushmen.

Glancing at this Late Quaternary culture as a whole, in view of the materials supplied on the European side, it will not be superfluous for me to call attention to two important points which some observers have shown a tendency to pass over.

Its successive phases, the Aurignacian, the Solutrean, and the Magdalenian, with its decadent Azilian offshoot—the order of which may now be regarded as stratigraphically established—represent, on the whole, a continuous story.

I will not here discuss the question as to how far the disappearance of Neanderthal Man and the close of the Moustierian epoch represents a "fault" or gap. But the view that there was any real break in the course of the cultural history of the Reindeer Age itself does not seem to have sufficient warrant.

It is true that new elements came in from more than one direction. On the old Aurignacian area, which had a trans-Mediterranean extension from Syria to Morocco, there intruded on the European side—apparently from the East—the Solutrean type of culture, with its perfected flint-working and exquisite laurel-leaf points. Magdalenian Man, on the other hand, great as the proficiency that he attained in the carving of horn and bone, was much behind in his flint-knapping. That there were dislocations and temporary set-backs is evident. But on every side we still note transitions and reminiscences. When, moreover, we turn to the most striking features of this whole cultural phase, the primeval arts of sculpture, engraving, and painting, we see a gradual upgrowth and unbroken tradition. From mere outline figures and simple two-legged profiles of animals we are led on step by step to the full freedom of the Magdalenian artists. From isolated or disconnected subjects we watch the advance to large compositions, such as the hunting scenes of the Spanish rock-paintings. In the culminating phase of this art we even find impressionist works. A brilliant illustration of such is seen in the galloping herds of horses, lightly sketched by the engraver on the stone slab from the Chaumont Grotto, depicting the leader in each case in front of his troop, and its serried line—straight as that of a well-drilled battalion—in perspective rendering. The whole must be taken to be a faithful memory sketch of an exciting episode of prairie life.

The other characteristic feature of the culture of the Reindeer Age that seems to deserve special emphasis, and is almost the corollary of the foregoing, is that it cannot be regarded as the property of a single race. It is true that the finely built Cro-Magnon race seems to have predominated, and must be regarded as an element of continuity throughout, but the evidence of the co-existence of other human types is clear. Of the physical characteristics of these it is not my province to speak. Here it will be sufficient to point out that their interments, as well as their general associations, conclusively show that they shared, even in its details, the common culture of the Age, followed the same fashions, plied the same arts, and were imbued with the same beliefs as the Cro-Magnon folk. The negroid skeletons intercalated in the interesting succession of hearths and interments of the Grotte des Enfantes at Grimaldi had been buried with the same rites, decked with the same shell ornaments, and were supplied with the same red colouring matter for use in the Spirit World, as we find in the other sepultures of these caves belonging to the Cro-Magnon race. Similar burial rites were associated in this country with the "Red Lady of Paviland," the contemporary Aurignacian date of which is now well established. A like identity of funeral custom recurred again in the sepulture of a man of the "Brünn" race on the Eastern boundary of this field of culture.

In other words, the conditions prevailing were analogous to those of modern Europe. Cultural features of the same general character had imposed themselves on a heterogeneous population. That there was a considerable amount of circulation, indeed — if not of primitive commerce—among the peoples of the Reindeer Age is shown by the diffusion of shell or fossil ornaments derived from the Atlantic, the Mediterranean, or from inland geological strata. Art itself is less the property of one or another race than has sometimes been imagined—indeed, if we compare those products of the modern carver's art that have most analogy with the horn and bone carvings of the Cave Men, and rise at times to great excellence—as we see them, for instance, in Switzerland or Norway—they are often the work of races of very different physical types. The negroid contributions, at least in the Southern zone of this Late Quaternary field, must not be underestimated. The early steatopygous images—such as some of these of the Balzi Rossi caves—may safely be regarded as due to this ethnic type, which is also pictorially represented in some of the Spanish rock-paintings.

The nascent flame of primeval culture was thus already kindled in that Older World, and, so far as our present knowledge goes, it was in the South-Western part of our Continent, on either side or the Pyrenees, that it shone its brightest. After the great strides in human progress already made at that remote epoch, it is hard, indeed, to understand what it was that still delayed the rise of European civilisation in its higher shape. Yet it had to wait for its fulfilment through many millennia. The gathering shadows thickened, and the darkness of a long night fell not on that favoured region alone, but throughout the wide area where Reindeer Man had ranged. Still the question rises—as yet imperfectly answered—were there no relay runners to pass on elsewhere the lighted torch?

Something, indeed, has been recently done towards bridging over the "hiatus" that formerly separated the Neolithic from the Palæolithic Age—the yawning gulf between two Worlds of human existence. The Azilian—a later decadent outgrowth of the preceding culture—which is now seen partially to fill the lacuna, seems to be in some respects an impoverished survival of the Aurignacian (Breuil, "Congr. Préhist," Geneva, 1912, p. 216). The existence of this phase was first established by the long and patient investigations of Piette in the stratified deposits of the Cave of Mas d'Azil in the Ariège, from which it derives its name, and it has been proved by recent discoveries to have had a wide extension. It affords evidence of a milder and moister climate—well illustrated by the abundance of the little wood snail (*helix nemoralis*), and the increasing tendency of the Reindeer to die out in the Southern parts of the area, so that in the fabric of the characteristic harpoons deer-horns are used as substitutes. Artistic designs now fail us, but the polychrome technique of the preceding Age still survives in certain schematic and geometric figures, and in curious coloured signs on pebbles. These last first came to light in the Cave of Mas d'Azil, but they have now been found to recur much further afield in a similar association in grottoes from the neighbourhood of Basel to that of Salamanca. So like letters are some of these signs that the lively imagination of Piette saw in them the actual characters of a primeval alphabet!

The little flakes with a worked edge often known as "pygmy flints," which were most of them designed for insertion into bone or horn harpoons, like some Neolithic examples, are very characteristic of this stratum, which is widely diffused in France and elsewhere under the misleading name of "Tardenoisan." At Ofnet, in Bavaria, it is associated with a ceremonial skull burial showing the co-existence at that spot of brachycephalic and dolichocephalic types, both of a new character. In Britain, as we know, this Azilian, or a closely allied phase, is traceable as far North as the Oban Caves.

What, however, is of special interest is the existence of a northern parallel to this cultural phase, first ascertained by the Danish investigator, Dr. Sarauw, in the Lake station of Maglemose, near the West coast of Zealand. Here bone harpoons of the Azilian type occur, with bone and horn implements showing geometrical and rude animal engravings of a character divergent from the Magdalenian tradition. The settlement took place when what is now the Baltic was still the great "Ancylus Lake," and the waters of the North Sea had not yet burst into it

It belongs to the period of the Danish pine and birch woods, and is shown to be anterior to the earliest shell mounds of the Kitchenmidden People, when the pine and the birch had given place to the oak. Similar deposits extend to Sweden and Norway, and to the Baltic Provinces as far as the Gulf of Finland. The parallel relationship of this culture is clear, and its remains are often accompanied with the characteristic "pygmy" flints. Breuil, however, while admitting the late Palæolithic character of this northern branch, would bring it into relation with a vast Siberian and Altaic province, distinguished by the widespread existence of rock-carvings of animals ("Les Subdivisions du Paléolithique Supérieur et leur Signification," *Congrès Intern. d'Anthrop. et d'Archéol. Préhist.*, XIV.me Sess., Genève, 1912, pp. 165, 238). It is interesting to note that a rock-carving of a reindeer, very well stylised, from the Trondhjem Fjord, which has been referred to the Maglemosian phase, preserves the simple profile rendering—two legs only being visible—of Early Aurignacian tradition.

It is worth noting that an art affiliated to that of the petroglyphs of the old Altaic region long survived in the figures of the Lapp troll-drums, and still occasionally lingers, as I have myself had occasion to observe, on the reindeer-horn spoons of the Finnish and Russian Lapps, whose ethnic relationship, moreover, points east of the Ural. The existence of a Late Palæolithic Province on the Russian side is, in any case, now well recognised, and itself supports the idea of a later shifting North and North-East, just as at a former period it had oscillated in a South-Western direction. All this must be regarded as corroborating the view long ago expressed by Boyd Dawkins that some part of the old Cave race may still be represented by the modern Eskimos ("Early Man in Britain," 1880, p. 233 *seqq.*). Testut's comparison of the short-statured Magdalenian skeleton from the rock shelter of Chancelade in the Dordogne with that of an Eskimo certainly confirms this conclusion.

On the other hand, the evidence, already referred to, of an extension of the Late Palæolithic culture to a North African zone, including rock-sculptures depicting a series of animals extinct there in the later age, may be taken to favour the idea of a partial continuation on that side. Some of the early rock-sculptures in the south of the continent, such as the figure of a walking elephant, reproduced by Dr. Peringuey, afford the clearest existing parallels to the best Magdalenian examples. There is much indeed to be said for the view, of which Sollas is an exponent, that the Bushmen, who at a more recent date entered that region from the North, and whose rock-painting attained such a high level of naturalist art, may themselves be taken as later representatives of the same tradition. In their human figures the resemblances descend even to conventional details, such as we meet with at Cogul and Alpera. Once more, we must never lose sight of the fact that from the Early Aurignacian Period onwards a negroid element in the broadest sense of the word shared in this artistic culture, as seen on both sides of the Pyrenees.

At least we now know that Cave Man did not suffer any sudden extinction, though on the European side, partly perhaps owing to the new climatic conditions, this culture underwent a marked degeneration. It may well be that, as the osteological evidence seems to imply, some outgrowth of the old Cro-Magnon type actually perpetuated itself in the Dordogne. We have certainly lengthened our knowledge of the Palæolithic. But in the present state of the evidence it seems better to subscribe to Cartailhac's view, that its junction with the Neolithic has not yet been reached. There does not seem to be any real continuity between the culture revealed at Maglemose and that of the immediately superposed Early Neolithic stratum of the shell-mounds, which moreover, as has been already said, evidence a change both in climatic and geological conditions, implying a considerable interval of time.

It is a commonplace of archæology that the culture of the Neolithic peoples throughout a large part of Central, Northern, and Western Europe—like the newly domesticated species possessed by them—is Eurasiatic in type. So, too, in Southern Greece and the Ægean world we meet with a form of Neolithic culture which must be essentially regarded as a prolongation of that of Asia Minor.

It is clear that it is on this Neolithic foundation that our later civilisation immediately stands. But in the constant chain of actions and reactions by which the history of mankind is bound together—short of the extinction of all concerned, a hypothesis in this case excluded—it is equally certain that no great human achievement is without its continuous effect. The more we realise the substantial amount of progress of the men of the Late Quaternary Age in arts and crafts and ideas, the more difficult it is to avoid the conclusion that somewhere "at the back of behind"—it may be by more than one route and on more than one continent, in Asia as well as Africa—actual links of connection may eventually come to light.

Of the origins of our complex European culture this much at least can be confidently stated: the earliest extraneous sources on which it drew lay respectively in two directions—in the Valley of the Nile on one side and in that of the Euphrates on the other.

Of the high early culture in the Lower Euphrates Valley our first real knowledge has been due to the excavations of De Sarzec in the Mounds of Tello, the ancient Lagash. It is now seen that the civilisation that we call Babylonian, and which was hitherto known under its Semitic guise, was really in its main features an inheritance from the earlier Sumerian race – culture in this case once more dominating nationality. Even the laws which Hammurabi traditionally received from the Babylonian Sun God were largely modelled on the reforms enacted a thousand years earlier by his predecessor, Urukagina, and ascribed by him to the inspiration of the City God of Lagash (see L. W. King, "History of Sumer and Akkad," p. 184). It is hardly necessary to insist on the later indebtedness of our civilisation to this culture in its Semitised shape, as passed on, together with other more purely Semitic elements, to the Mediterranean world through Syria, Canaan, and Phœnicia, or by way of Assyria, and by means of the increasing hold gained on the old Hittite region of Anatolia.

Even beyond the ancient Mesopotamian region which was the focus of these influences the researches of De Morgan, Gautier, and Lampre, of the French "Délégation en Perse," have opened up another independent field, revealing a nascent civilisation equally ancient, of which Elam (the later Susiana) was the centre. Still further afield, moreover, some three hundred miles east of the Caspian, the interesting investigations of the Pumpelly Expedition in the mounds of Anau, near Ashkabad, in Southern Turkestan, have brought to light a parallel and related culture. The painted Neolithic sherds of Anau, with their geometrical decoration, similar to contemporary ware of Elam, have suggested wide comparisons with the painted pottery of somewhat later date found in Cappadocia and other parts of Anatolia, as well as in the North Syrian regions. It has, moreover, been reasonably asked whether another class of painted Neolithic fabrics, the traces of which extend across the Steppes of Southern Russia, and by way of that ancient zone of migration to the lower Danube and Northern Greece, may not stand in some original relation to the same ancient province. The new discoveries, however, in the mounds of Elam and Anau have at most a bearing on the primitive phase of culture in parts of South-Eastern Europe that preceded the age when metal was generally in use.

Turning to the Nile Valley we are again confronted with an extraordinary revolution in the whole point of view effected during recent years. Thanks mainly to the methodical researches initiated by Flinders Petrie, we are able to look back beyond the Dynasties to the very beginnings of Egyptian civilisation. Already by the closing phase of the Neolithic and by the days of the first incipient use of metals the indigenous population had attained an extraordinarily high level. If on the one hand it displays Libyan connexions, on the other we already note the evidences of commercial intercourse with the Red Sea; and the constant appearance of large rowing vessels in the figured designs shows that the Nile itself was extensively used for navigation. Flint working was carried to unrivalled perfection, and special artistic refinement was displayed in the manufacture of vessels of variegated breccia and other stones. The antecedent stages of many Egyptian hieroglyphs are already traceable, and the cult of Egyptian divinities, like Min, was already practised. Whatever ethnic change may have marked the establishment of Pharaonic rule, here, too, the salient features of the old indigenous culture were taken over by the new régime. This early Dynastic period itself has also received entirely new illustration from the same researches, and the freshness and force of its artistic works in many respects outshine anything produced in the later course of Egyptian history.

The continuity of human tradition as a whole in areas geographically connected like Eurafrica on the one side and Eurasia on the other has been here postulated. Since, as we have seen, the Late Palæolithic culture was not violently extinguished but shows signs of survival both North and South, we are entitled to trace elements of direct derivation from this source among the inherited acquirements that finally led up to the higher forms of ancient civilisation that arose on the Nile and the Euphrates. In many directions, we may believe, the flaming torch had been carried on by the relay runners.

But what, it may be asked, of Greece itself, where human culture reached its highest pinnacle in the Ancient World and to which we look as the principal source of our own civilisation?

Till within recent years it seemed almost a point of honour for classical scholars to regard Hellenic civilisation as a Wonder-Child, sprung, like Athena herself, fully panoplied from the head of Zeus. The indebtedness to Oriental sources was either regarded as comparatively late or confined to such definite borrowings as the alphabet or certain weights and measures. Egypt, on the other hand, at least till Alexandrine times, was looked on as something apart, and it must be said that Egyptologists on their side were only too anxious to preserve their sanctum from profane contact.

A truer perspective has now been opened out. It has been made abundantly clear that the rise of Hellenic civilisation was itself part of a wider economy and can be no longer regarded as an isolated phenomenon. Indirectly its relation to the greater World and to the ancient centres to the South and East has been now established by its affiliation to the civilisation of prehistoric Crete and by the revelation of the extraordinarily high degree of proficiency that was there attained in almost all departments of human art and industry. That Crete itself—the "Mid-Sea land," a kind of halfway house between three continents—should have been the cradle of our European civilisation was, in fact, a logical consequence of its geographical position. An outlier of Mainland Greece, almost opposite the mouths of the Nile, primitive intercourse between Crete and the further shores of the Libyan Sea was still further facilitated by favourable winds and currents. In the Eastern direction, on the other hand, island stepping-stones brought it into easy communication with the coast of Asia Minor, with which it was actually connected in late geological times.

But the extraneous influences that were here operative from a remote period encountered on the island itself a primitive indigenous culture that had grown up there from immemorial time. In view of some recent geological calculations, such as those of Baron De Geer, who by counting the number of layers of mud in Lake Ragunda has reduced the ice-free period in Sweden to 7000 years, it will not be superfluous to emphasise the extreme antiquity that seems to be indicated for even the later Neolithic in Crete. The Hill of Knossos, upon which the remains of the brilliant Minoan civilisation have found their most striking revelation, itself resembles in a large part of its composition a great mound or Tell—like those of Mesopotamia or Egypt—formed of layer after layer of human deposits. But the remains of the whole of the later ages represented down to the earliest Minoan period (which itself goes back to a time contemporary with the early Dynasties of Egypt at a moderate estimate to 3400 B.C.) occupy considerably less than a half—19 feet, that is, out of a total of over 45 ft. Such calculations can have only a relative value, but, even if we assume a more rapid accumulation of débris for the Neolithic strata, and deduct a third from our calculation, they would still occupy a space of over 3400 years, giving a total antiquity of some 9000 years from the present time." (For a fuller statement I must refer to my forthcoming work, "The Nine Minoan Periods," Macmillans; Vol. I., "Neolithic Section"). No Neolithic section in Europe can compare in extent with that of Knossos, which itself can be divided by the character of its contents into an Early, Middle, and Late phase. But its earliest stratum already shows the culture in an advanced stage, with carefully ground and polished axes and finely burnished pottery. The beginnings of Cretan Neolithic must go back to a still more remote antiquity.

The continuous history of the Neolithic Age is carried carried back at Knossos to an earlier epoch than is represented in the deposits of its geographically related areas on the Greek and Anatolian side. But sufficient materials for comparison exist to show that the Cretan branch belongs to a vast Province of primitive culture that extended from Southern Greece and the Ægean islands throughout a wide region of Asia Minor, and probably still further afield.

An interesting characteristic is the appearance in the Knossian deposits of clay images of squatting female figures of a pronouncedly steatopygous conformation, and with hands on the breasts. These in turn fit on to a large family of similar images which recur throughout the above area, though elsewhere they are generally known in their somewhat developed stage, showing a tendency to be translated into stone, and finally—perhaps under extraneous influences both from the North and East—taking a more extended attitude. These clearly stand in a parallel relationship to a whole family of figures with the organs of maternity strongly developed that characterise the Semitic lands, and which seem to have spread from there to Sumeria and to the seats of the Anau culture.

At the same time this steatopygous family, which in other parts of the Mediterranean basin ranges from prehistoric Egypt and Malta to the North of Mainland Greece, calls up suggestive reminiscences of the similar images of Aurignacian Man. It is especially interesting to note that in Crete, as in the Anatolin region where these primitive images occur, the worship of a Mother Goddess predominated in later times, generally associated with a divine Child—a worship which later survived in a classical guise and influenced all later religion. Another interesting evidence of the underlying religious community between Crete and Asia Minor is the diffusion in both areas of the cult of the Double Axe. This divine symbol, indeed, or "Labrys," became the special emblem of the Palace sanctuary of Knossos itself, which owes to it its traditional name of Labyrinth. I have already called attention to the fact that the absorptive and disseminating power of the Roman Empire brought the cult of a male form of the divinity of the Double Axe to the Roman Wall, and to the actual site on which Newcastle stands.

The fact should never be left out of sight that the gifted indigenous stock which in Crete eventually took to itself, on one hand, and the other so many elements of exotic culture was still deep-rooted in its own. It had, moreover, the advantages of an insular people in taking what it wanted, and no more. Thus it was stimulated by foreign influences but never dominated by them, and there is nothing of the servility of Phœnician art. Much as it assimilated, it never lost its independent tradition.

It is interesting to note that the first quickening impulse came to Crete from the Egyptian and not from the Oriental side—the Eastern factor, indeed, is of comparatively late appearance. My own researches have led me to the definite conclusion that cultural influences were already reaching Crete from beyond the Libyan Sea before the beginning of the Egyptian Dynasties. These primitive influences are attested, amongst other evidences, by the forms of stone vessels, by the same æsthetic tradition in the selection of materials distinguished by their polychromy, by the appearance of certain symbolic signs, and the subjects of shapes and seals which go back to prototypes in use among the "Old Race" of the Nile Valley. The impression of a very active agency, indeed, is so strong that the possibility of some actual immigration into the island of the older Egyptian element, due to the conquests of the first Pharaohs, cannot be excluded.

The continuous influence of Dynastic Egypt from its earliest period onwards is attested both by objects of import and their indigenous imitations, and an actual monument of a Middle Empire Egyptian was found in the Palace Court at Knossos. More surprising still are the cumulative proofs of the reaction of this early Cretan civilisation on Egypt itself, as seen not only in the introduction there of such beautiful Minoan fabrics as the elegant polychrome vases, but in the actual impress observable on Egyptian Art even on its religious side. The Egyptian griffin is fitted with Minoan wings. So, too, on the other side we see the symbols of Egyptian religion impressed into the service of the Cretan Nature Goddess. who in certain respects was partly assimilated with Hathor, the Egyptian Cow-Goddess of the Underworld.

My own most recent investigations have more and more brought home to me the all-pervading community between Minoan Crete and the land of the Pharaohs. When we realise the great indebtedness of the succeeding classical culture of Greece to its Minoan predecessor the full significance of this conclusion will be understood. Ancient Egypt itself can no longer be regarded as something apart from general human history. Its influences are seen to lie about the very cradle of our own civilisation.

The high early culture, the equal rival of that of Egypt and Babylonia, which thus began to take its rise in Crete in the fourth millennium before our era, flourished for some two thousand years, eventually dominating the Ægean and a large part of the Mediterranean basin. To the civilisation as a whole I ventureed, from the name of the legendary King and law-giver of Crete, to apply the name of "Minoan," which has received general acceptance, and it has been possible now to divide its course into three Ages—Early, Middle, and Late, answering roughly to the successive Egyptian Kingdoms, and each in turn with a triple sub-division.

It is difficult, indeed, in a few words to do adequate justice to this earliest of European civilisations. Its achievements are too manifold. The many-storeyed palaces of the Minoan priest-kings in their great days, by their ingenious planning, their successful combination of the useful with the beautiful and stately, and, last but not least, by their scientific sanitary arrangements. far outdid the similar works, on however vast a scale, of Egyptian or Babylonian builders. What is more, the same skilful and commodious construction recurs in a whole series of private mansions and smaller dwellings throughout the island. Outside "broad Knossos" itself, flourishing towns sprang up far and wide on the country sides. New and refined crafts were developed, some of them, like that of the inlaid metal work, unsurpassed in any age or country. Artistic skill, of course, reached its acme in the great palaces themselves, the corridors, landings, and porticoes of which were decked with wall paintings and high reliefs, showing in the treatment of animal life not only an extraordinary grasp of Nature, but a grandiose power of composition such as the world had never seen before. Such were the great bull-grappling reliefs of the Sea Gate at Knossos and the agonistic scenes of the great Palace hall.

The modernness of much of the life here revealed to us is astonishing. The elaboration of the domestic arrangements, the staircases storey above storey, the front places given to the ladies at shows, their fashionable flounced robes and jackets, the gloves sometimes seen on their hands or hanging from their folding chairs, their very mannerisms as seen on the frescoes, pointing their conversation with animated gestures—how strangely out of place would it all appear in a classical design! Nowhere, not even at Pompeii, have more living pictures of ancient life been called up for us than in the Minoan Palace of Knossos. The touches supplied by its closing scene are singularly dramatic—the little bath-room opening out of the Queen's parlour, with its painted clay bath, the royal draught-board flung down in the court, the vessels for anointing and the oil-jar for their filling ready to hand by the throne of the Priest-King, with the benches of his Consistory round and the sacral griffins on either side. Religion, indeed, entered in at every turn. The palaces were also temples, the tomb a shrine of the Great Mother. It was perhaps owing to the religious control of art that among all the Minoan representations—now to be numbered by thousands—no single example of indecency has come to light.

A remarkable feature of this Minoan civilisation cannot be passed over. I remember that at the Liverpool Meeting of this Association in 1896—just before the first results of the new discoveries in Crete were known—a distinguished archæologist took as the subject of an evening lecture "Man before Writing," and, as a striking example of a high culture attained by "*Analfabeti*," singled out that of Mycenæ—a late offshoot, as we know now, from Minoan Crete. To such a conclusion, based on negative evidence, I confess I could never subscribe—for had not even the people of the Reindeer Age attained to a considerable proficiency in expression by means of symbolic signs? To-day we are able to trace the gradual evolution on Cretan soil of a complete system of writing from its earliest pictographic, through a conventionalised hieroglyphic to a linear stage of great perfection. In addition to inscribed sealings and other records some two thousand clay tablets have now come to light, mostly inventories or contracts; for though the script itself is still undeciphered the pictorial figures that often appear on these documents supply a valuable clue to their contents. The numeration also is clear, with figures representing sums up to 10,000. The inscribed sealings, signed, counter-marked, and countersigned by controlling officials, gave a high idea of the elaborate machinery of Government and Administration under the Minoan rulers.

The minutely organised legal conditions to which this points confirm the later traditions of Minos, the great law-giver of prehistoric Crete, who, like Hammurabi and Moses, was said to have received the law from the God of the Sacred Mountain. The clay tablets themselves were certainly due to Oriental influences, which make themselves perceptible in Crete at the beginning of the Late Minoan Age, and may have been partly resultant from the reflex action of Minoan colonisation in Cyprus. From this time onwards Eastern elements are more and more traceable in Cretan culture, and are evidenced by such phenomena as the introduction of chariots—themselves perhaps more remotely of Aryan-Iranian derivation—and by the occasional use of cylinder seals.

Simultaneously with its Eastern expansion, which affected the coast of Phœnicia and Palestine as well as Cyprus, Minoan civilisation now took firm hold of Mainland Greece, while traces of its direct influence are found in the West Mediterranean basin—in Sicily, the Balearic Islands, and Spain. At the time of the actual Conquest and during the immediately succeeding period the civilisation that appears at Mycenæ and Tiryns, at Thebes and Orchomenos, and at other centres of Mainland Greece, though it seems to have brought with it some already assimilated Anatolian elements, is still in the broadest sense Minoan. It is only at a later stage that a more provincial offshoot came into being to which the name Mycenæan can be properly applied. But it is clear that some vanguard at least of the Aryan Greek immigrants came into contact with this high Minoan culture at a time when it was still in its most flourishing condition. The evidence of Homer itself is conclusive. Arms and armour described in the poems are those of the Minoan prime, the fabled shield of Achilles, like that of Herakles described by Hesiod, with its elaborate scenes and variegated metalwork, reflects the masterpieces of Minoan craftsmen in the full vigour of their art; the very episodes of epic combat receive their beat illustration on the signets of the great days of Mycenæ. Even the lyre to which the minstrel sang was a Minoan invention. Or, if we turn to the side of religion, the Greek temple seems to have sprung from a Minoan hall, its earliest pediment schemes are adaptations from the Minoan tympanum—such as we see in the Lions' Gate—the most archaic figures of the Hellenic Goddesses, like the Spartan Orthia, have the attributes and attendant animals of the great Minoan Mother.

Some elements of the old culture were taken over on the soil of Hellas. Others which had been crushed out in their old centres survived in the more Eastern shores and islands formerly dominated by Minoan civilisation, and were carried back by Phœnician or Ionian intermediaries to their old homes. In spite of the overthrow which about the twelfth century before our era fell on the old Minoan dominion and the onrush of the new conquerers from the North, much of the old tradition still survived to form the base for the fabric of the later civilisation of Greece. Once more, through the darkness, the lighted torch was carried on, the first glimmering flame of which had been painfully kindled by the old Cave dwellers in that earlier Palæolithic World.

The Roman Empire, which in turn appropriated the heritage that Greece had received from Minoan Crete, placed civilisation on a broader basis by welding together heterogeneous ingredients and promoting a cosmopolitan ideal. If even the primeval culture of the Reindeer Age embraced more than one race and absorbed extraneous elements from many sides, how much more is that the case with our own, which grew out of the Greco-Roman! Civilisation in its higher form to-day, though highly complex, forms essentially a unitary mass. It has no longer to be sought out in separate luminous centres, shining like planets through the surrounding night. Still less is it the property of one privileged country or people. Many as are the tongues of mortal men, its votaries, like the Immortals, speak a single language. Throughout the whole vast area illuminated by its quickening rays, its workers are interdependent, and pledged to a common cause.

We, indeed, who are met here to-day to promote in a special way the Cause of Truth and Knowledge, have never had a more austere duty set before us. I know that our ranks are thinned. How many of those who would otherwise be engaged in progressive research have been called away for their country's service! How many who could least be spared were called to return no more! Scientific intercourse is broken, and its cosmopolitan character is obscured by the death struggle in which whole Continents are locked. The concentration, moreover, of the Nation and of its Government on immediate ends has distracted it from the urgent reforms called for by the very evils that are the root cause of many of the greatest difficulties it has had to overcome. It is a lamentable fact that beyond any nation of the West the bulk of our people remains sunk not in comparative ignorance only—for that is less difficult to overcome—but in intellectual apathy. The dull incuria of the parents as reflected in the children, and the desire for the acquirement of knowledge in our schools and colleges is appreciably less than elsewhere. So, too, with the scientific side of education, it is not so much the actual amount of Science taught that is in question—insufficient as that is—as the instillation of the scientific spirit itself—the perception of method, the sacred thirst for investigation.

But can we yet despair of the educational future of a people that has risen to the full height of the great emergency with which they were confronted? Can we doubt that, out of the crucible of fiery trial, a New England is already in the moulding?

We must all bow before the hard necessity of the moment. Of much we cannot judge. Great patience is demanded. But let us, who still have the opportunity of doing so, at least prepare for the even more serious struggle that must ensue against the enemy in our midst, that gnaws our vitals. We have to deal with ignorance, apathy, the non-scientific mental attitude, the absorption of popular interest in sports and amusements.

And what, meanwhile, is the attitude of those in power—of our Government, still more of our permanent officials? A cheap epigram is worn threadbare in order to justify the ingrained distrust of expert, in other words of scientific, advice on the part of our public offices. We hear, indeed, of "Commissions" and "Enquiries," but the inveterate attitude of our rulers towards the higher interests that we are here to promote is too clearly shown by a single episode. It is those higher interests that are the first to be thrown to the wolves. All are agreed that special treasures should be stored in positions of safety, but at a time when it might have been thought desirable to keep open every avenue of popular instruction and of intelligent diversion, the galleries of our National Museum at Bloomsbury were entirely closed for the sake of the paltriest saving—three minutes, it was calculated, of the cost of the War to the British Treasury! That some, indeed, were left open elsewhere was not so much due to the enlightened sympathy of our politicians, as to their alarmed interests in view of the volume of intelligent protest. Our friends and neighbours across the Channel, under incomparably greater stress, have acted in a very different spirit.

It will be a hard struggle for the friends of Science and Education, and the air is thick with mephitic vapours. Perhaps the worst economy to which we are to-day reduced by our former lack of preparedness is the economy of Truth. Heaven knows!—it may be a necessary penalty. But its results are evil. Vital facts that concern our national well-being, others that even affect the cause of a lasting Peace, are constantly suppressed by official action. The negative character of the process at work which conceals its operation from the masses makes it the more insidious. We live in a murky atmosphere admidst the suggestion of the false, and there seems to be a real danger that the recognition of Truth as itself a Tower of Strength may suffer an eclipse.

It is at such a time and under these adverse conditions that we, whose object it is to promote the Advancement of Science, are called upon to act. It is for us to see to it that the lighted torch handed down to us from the Ages shall be passed on with a still brighter flame. Let us champion the cause of Education, in the best sense of the word, as having regard to its spiritual as well as its scientific side. Let us go forward with our own tasks, unflinchingly seeking for the Truth, confident that, in the eternal dispensation, each successive generation of seekers may approach nearer to the goal.

Magna est veritas, et prævalebit.

Institute of Metals.—The Autumn Meeting of the Institute will be held in the Rooms of the Chemical Society, Burlington House, Piccadilly, W., on Wednesday, September 20, commencing at 4 p.m. A selection of papers will be read and discussed.

THE EXAMINATION OF CHINESE WOOD OIL.

By FRANK BROWNE, F.I.C., Formerly Government Analyst, Hongkong.

Since the publication of a heat test (Chemical News, July 12, 1912) much has been done in order to arrive at an acceptable method of examination. In the first place a quantity of genuine nuts were obtained from Wuchow, Kwangsi Province, and a quantity of oil was extracted by pressure only. Specimens of the nuts and of the extracted oil were sent to several authorities in various parts of the world. This pure oil had the following characters:—

Specific gravity, 15°/15°	0·9415
Iodine value	167
Saponification value	191
Heat test..	12 minutes
Refractive index at 20° C	1·5206
" " 15° C	1·5226

At that time (1912) there was no definite system of sampling the commercial oil, and in consequence there were disputes, mostly with buyers in the United States, as to the quality of some of the consignments. These disturbances at last became so frequent as to seriously interfere with the export trade. The matter received the attention of the Association of Exporters and Dealers of Hongkong, which, with the assistance of the local government, endeavoured to place the sale of this oil on a more satisfactory footing.

From the characters of the pure oil extracted in the Government Laboratory and from the results of numerous examinations of oils, which had been accepted by buyers as genuine and thoroughly satisfactory, the following specification was drawn up for South China Wood Oil:—

1. Chinese wood oil shall be pale in colour (according to season's production), merchantably free from foots, dirt, and moisture. The total impurities shall not exceed 1 per cent, but unless otherwise provided for impurities not plainly adulterations up to 5 per cent shall not justify rejection, but allowance shall be made by sellers for such impurities in excess of 1 per cent.
2. The refractive index of such oil shall not be less than 1·5204 at 15° C. Minus 0·0004 shall be considered the correction for each degree C. above 15 to 35° C., which should be applied to the refractive index when such is determined at temperatures between the points stated.
3. The specific gravity at 15° C. shall not be less than 0·9400.
4. The oil shall satisfy the requirements of either Worstall's,* Bacon's,* Browne's (Chemical News, July 12, 1912 – the period of setting in this heat test not to exceed thirteen minutes), or Chapman's (*Analyst*, Dec., 1912) heat test.

Any sample of South China wood oil that satisfies all the four tests above, namely, Nos. 1, 2, 3, and any one of the heat tests in No. 4, shall be considered to be good South China wood oil free from adulteration.

Particulars of this specification were sent by the Association to responsible bodies in several countries, and at the same time opinions were asked for as to any amendment desired. The replies received did not seem to indicate the necessity for any change in the specification as described above. The Hongkong Government then undertook the sampling and examination of the oil. This consists in drawing about an ounce from each cask of oil offered for sale. The refractive index of each quantity is first determined, and any cask of oil with a refractive index under the specification figure is condemned for export purposes. The approved samples are then bulked and the gravity and heat test of the mixture determined. If the oil passes these tests the casks are sealed with lead seals, bearing a Government impression, and are then ready for shipment. The institution of this system of sampling has proved most satisfactory. It has restored the sale of the oil to its former dimensions, it has raised its quality, and has put an end to vexatious disputes and expensive arbitrations.

The following points may be useful to those examining this oil:—

When the gravity is determined at a temperature other than 15° C. it has been found that 0·00064 is the correction for 1° C. Thus a gravity of 0·9401 at 20°/15° C. is 0·9433 at 15°/15° C.

It should be noted also that in the heat test described in the previous paper a thermometric correction is made for the cool column. It is very important to apply this. For the sake of obtaining uniformity in results it may be mentioned that the formula used was—

$$T + 0{\cdot}00016\,(T - t)\,N,$$

where T was the observed temperature, t the mean temperature of the emergent column, and N the number of scale degrees of the emergent column.

My thanks are due to Mr. A. C. Franklin, F.I.C., for extracting the pure oil and determining several constants, and to Mr. E. R. Dovey, A.R.C.S., for making a large number of observations on its refractive index at various temperatures.

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* Described in the rules regulating business among members of the New York Produce Exchange in vegetable oils and fats not otherwise provided for as amended on September 5, 1912.

WASTE PINE WOOD UTILISATION.

By JOHN E. TEEPLE.

This is an old, old industry. As far back as we have definite information people were using tar on their cordage and pitch on their ships. Even Noah's Ark you recall was "pitched within and pitched without," and the ark of bulrushes that supported the baby Moses was "daubed with pitch." We lack positive assurance that a pure pine pitch was used in these cases, but it may easily have been cypress pitch, which is not so widely different. Since the industry is such an old one the chemist is not to be either censured or credited with its results until within the last thirty years, and more especially within the last ten or fifteen years. The method commonly used formerly was to pile the wood in large heaps, cover it with earth, and by burning a portion of the wood accomplish a destructive distillation of the remainder. The products were tar and charcoal, although some few attempts were made to recover the volatile spirit for use as an illuminant.

About thirty years ago the use of iron retorts was introduced, and this made possible the recovery of an unsatisfactory turpentine, a little of the natural pine oils, and considerable tar oil, creosote oil, pitch, and pyroligneous acid, in addition to tar and charcoal. The turpentine had a vicious odour, but being in small amount it could usually be worked off by persuasion. Tar was a standard commodity, but the trade soon began to differentiate between this retort tar and ordinary kiln tar, and the purchaser demanded a reduction in the case of the former or refused it. Charcoal could be sold for household fuel provided the plant was located in the neighbourhood of a fair-sized city. Otherwise it was used to fire the retorts. Gas was also at a time recovered and burned under retorts. When pitch was not readily saleable it could be dissolved in the tar oils or creosote oils and sold as tar, but these various light and heavy distillation oils accumulated, and depending on his ingenuity the manufacturer worked them up into paint oils, mixed paints, insecticides, disinfectants, fungicides, embalming fluids, medicinal products, and so on until the catalogue becomes alarmingly long. This destructive distillation industry still exists. It is one of the two methods of treating wood to obtain naval stores that has been able to operate continuously even under the present very adverse conditions. Many improvements have been made in the type of the retort, in the regulation of heat, and in the separation and preparation of products for the market. In many cases the turpentine now obtained is of excellent odour and of surprisingly good quality, but its success has usually depended on the ability of the manufacturer to work up his oils into lines of specialities under carefully established trade names, and thus protect himself from too vigorous competition. He has improved his retort tar so that now it commonly commands the same price as kiln tar, and is sometimes quoted at a higher figure. With the present high prices ruling for acetate of lime, due to the strong demand for acetone, he is even proceeding in some instances to the manufacture of this product from his pyroligneous acid. A considerable part of these improvements has of course been due to chemists, but it must be admitted that a further very considerable part of the preparation of products for the market has been due rather to business men who are good observers but were not primarily trained as chemists. It seems to me that the destructive distillation of wood is wrong in principle, with our present knowledge of its composition, but at the same time the fact that some of these plants have been continuously operating for many years indicates that they are not to be abolished with the speed that advocates of some of the newer processes have assured us.

Of other processes that have been suggested—distillation with superheated steam, extraction with rosin bath or tar and pitch bath, distillation with water, distillation with hot gases, digestion with soda and application of vacuum—have all had their trial in a commercial way, and a number of them have seemed to operate successfully for a while, due usually to special market conditions, but for the present these have all passed into history. It is very doubtful whether any of them will appear again, at least alone, even under improved conditions. While they lasted each one found vigorous supporters and provoked much discussion. The question, for example, whether the steam should preferably pass upward or downward through a retort was considered of considerable moment, but now it hardly arouses our interest. Some chemist usually took an active part in developing all of these processes, but the fact that none of them are operating to-day should not be laid entirely against him. In many cases he was responsible only for the laboratory results, and plants were constructed without the aid of chemical engineers, or in fact of chemists or engineers of any kind. In many other cases he had no first-hand knowledge of the industry himself, and relied on faulty information as to cost of wood and market conditions, supplied by men who were promoting the plants. In any case in developing these processes the chemist and chemical engineer accumulated and frequently put on record a fund of very valuable information, which is not at all lost, but which will have an important bearing on the future development of the industry.

In one important respect the chemist performed valuable service during this period of development. For the first time there was produced under his supervision a quantity of wood turpentine and pine oil sufficient to have an appreciable effect on the market. He succeeded in making a wood turpentine of a much higher and more uniform grade than had ever been attained before, and by his knowledge of its uses he overcame the prejudice against it, due to its different odour and different source, in enough places so that a firm and steady outlet on good prices was obtained for all that could be supplied. For the first time, too, there was a very considerable amount of the heavy natural oils of the wood, known as pine oil, to be disposed of. This had no regular market, and he succeeded in finding a use for it in a very wide range of industries, where it has so firmly established its value that at the present time the supply cannot begin to equal the demand.

The one other process which has apparently proved of value, and which is still in operation to day under adverse market conditions in at least two or three plants, is that of extraction by means of a volatile solvent. This method was at one time very extensively employed, producing more naval stores from waste wood than all other systems combined. The amounts of turpentine and pine oil were large and of good quality, and one new product was added from the wood—rosin. This was ultimately refined to a grade approximately corresponding to F and G grades of gum rosin. At first progress in marketing this was rather difficult, but the oils and tarry matters affecting its use were in part eliminated, and in part the customer was taught what changes were necessary in order to use it as satisfactorily as gum rosins, so that to-day again the demand exceeds the supply.

The worst feature, of course, in the development of this industry during the last few years has been the wide fluctuation in prices. In 1911 F rosin reached a high price of 8.45 dols. per barrel of 280 lbs. at Savannah; to-day it is 3 dols., scarcely more than one-third of the high figure, and it has been lower. In 1911 turpentine reached a high price of 1.07 dols. per gallon at Savannah; to-day it is 38 c., and has been lower. Most of these plants were built on the assumption that turpentine would not go below 50c. per gallon nor rosin below 5 dols. These conditions were freely predicted at the time by people who had spent their lives in the naval stores industry, and so probably the chemist should not be blamed too much for the failure of processes to operate successfully at much lower figures when he had based all his calculations on the higher figures and on the best judgment of people well informed as to conditions.

Now as to the future of the industry. Let us look first at the composition of the material with which we have to deal. Assuming that this is what we know as fat lightwood or as fat lightwood stumps, it contains rosin, turpentine, pine oil, and the wood fibre. The problem is, In what way can all these products be extracted and placed on the market to bring the largest net amount to the manufacturer? In some places, where the timber has been very largely the long-leaf pine, there is the additional factor of so locating his plant that he can entirely clear the land and largely enhance its value at the same time that he is furnishing his plant with raw material. In the future this will, no doubt, have an important bearing on the establishment of plants, but it will not be considered here. Suppose we have 5000 lbs. of very rich fat lightwood stumps. Suppose this contains 20 per cent, or 1000 lbs., of rosin; 40 gallons, or 300 lbs., of turpentine and pine oil, and 15 per cent., or 750 lbs., of water. This leaves nearly 3000 lbs of wood fibre. Now if we subject this 5000 lbs. of fat lightwood to destructive distillation, no matter how carefully, we shall not get all the turpentine and we get only a small portion of the pine oil before the rosin and the wood itself begin to decompose. The rosin would be valuable if we could get it, or its decomposition product, rosin oil. The pine oil would be valuable if we could get it, but before either the rosin oil or the pine oil leave the retort in any quantity they become thoroughly mixed with the tar and tar oils from the decomposition of the wood fibre, and there is no convenient way of ever separating them again in marketable condition from the resulting mess. If we investigate any of the other methods that have been discussed above we find an important loss in some one or more of the products originally present in the wood. If we digest with soda there is a very fair recovery of the turpentine and a moderately good recovery of the pine oil, but the rosin and resinate are not in good marketable condition, and it would be very difficult to get them in any condition for anything but very special markets. On the other hand, if we use a volatile solvent, properly selected and properly applied, we can recover nearly the whole of the rosin, turpentine, and pine oil, and have left the wood fibre unchanged. The rosin, the turpentine, and the pine oil will be in such a condition that they can be made into the best grades it is possible to produce from wood. The wood fibre is free of rosin and is in just the condition required for digestion to manufacture wood pulp. According to information and experiments, it gives a good yield of a very strong-fibred pulp. Probably it will work up best into what is known as Kraft pulp, or undercooked pulp, and this 3000 lbs. of wood fibre remaining should furnish about 1500 lbs. of good marketable pulp.

Our wood fibre has two disadvantages as a source of pulp. In the first place it cannot be entirely freed from the charcoal and charred and burned wood, and in the second place it will not be entirely free from bark, but there is no question that it will produce a good grade of brown wrapping paper, and with this addition we have made a very complete utilisation of our 5000 lbs. of wood. The difficulty heretofore has been that the naval stores manufacturer has approached the problem with the view of making the wood-pulp plant an annexe to his existing plant. The wood-pulp plant is the more expensive, requires the more skilled labour, and is by far the more important, so that the rosin and turpentine production should be considered rather as an annexe to the pulp plant, or, better still, the whole should be considered as one complete proposition. Many people have this combination of rosin, turpentine, pine oil, and wood pulp in their minds at the present time. There is no doubt that it will be tried before long. It is only to be hoped that when it does receive its trial it will be under the supervision of men thoroughly acquainted with both the wood-pulp industry and the wood-extraction industry, and with the aid of the most competent chemical engineers there are available. In this way it can build on the mistakes of its predecessors, and it seems to me to stand an excellent prospect of success. There has too much good work gone into this industry and there is too much accumulated information available to allow it to languish. I feel sure it has an important future, and when its success ultimately comes very large credit will be due to the chemists and chemical engineers who have made it possible.—*Journal of Industrial and Engineering Chemistry*, vii., No. 11.

USES OF TUNGSTEN.

The great use of tungsten is as an alloy of high-speed steel—that is, steel used for making tools used in metal-turning lathes running at high speed—to which tungsten imparts the property of holding its temper at higher temperatures than will carbon steels. In such steels from 16 to 20 per cent of tungsten is used. Saw blades are made which contain 1 to 2 per cent tungsten. The use of tungsten in magnet steels has consumed large quantities, but this use seems to be declining somewhat. The now well-known ductile tungsten is used for incandescent lamps, which are fast displacing carbon lamps. Lately greatly improved lamps, in which the wire is wound in helices and in which the globes are filled with nitrogen, have brought the consumption of electricity down to 0·4—0·5 watt per candle and have produced a close approach to white light. These lamps are furnished in candle powers up to 2000. Undoubtedly the bulk of the research in the manufacture and use of ductile metallic tungsten has been carried out by the highly efficient corps of scientists under the direction of Dr. W. R. Whitney in the General Electric Company's wonderful research laboratories. Dr. C. G. Fink, of the company's staff, in a paper delivered before the Section of Electro-Chemistry, Eighth International Congress, Applied Chemistry, September 6, 1913 (*Metall. and Chem. Eng.*, 1912, x., 580), gives the probable or possible uses of worked tungsten as follows:—

The ductile metal is practically insoluble in all of the common acids; its melting-point is higher than that of any other metal; its tensile strength exceeds that of iron and nickel; it is paramagnetic; it can be drawn to smaller sizes than any other metal, and its specific gravity is 70 per cent higher than that of lead. It was natural that a metal with such striking properties as these should soon find application other than that for incandescent lamps.

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, &c. The service far exceeds that for platinum and platinum-iridium contacts due to the greater hardness, higher heat conductivity, and lower vapour pressure of tungsten as compared with platinum.

Electric laboratory furnaces with tungsten resisters are of two types. In one a tungsten wire is wound on an aluminium tube in an air-tight box with a hydrogen atmosphere. In the second a tungsten metal tube takes the place of the helical carbon resister in an Arsem vacuum furnace.

Tungsten gauze is used successfully for separating solids from acid liquids in the laboratory. This gauze could well be used on a commercial scale; for example, for the removal of sludge from copper refining baths and for centrifugal apparatus in general whenever acid liquids or acid gases are dealt with. Furthermore, it might be used in apparatus such as described by Cottrell for the removal of sulphuric mist from gases.

Wrought tungsten targets for Röntgen tubes have proved to be one of the most interesting applications.

For thermocouples the tungsten-molybdenum couple is not less interesting. The electromotive force increases with the temperature up to about 540° C. (12½ millivolts), then decreases and passes through 0 millivolts at about 1300° C. This couple is very convenient for high-temperature measurements in the tungsten-hydrogen furnace.

For standard weights tungsten is also well suited, since wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore, the density is high (19·3 to 21·4) and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

Besides the applications of tungsten cited above, many others have been but partly worked out and others merely suggested. Owing to its chemical stability the finest sizes of wire down to 0·0002 inch, or 0·0005 mm. in diameter, are well adapted for galvanometer suspensions and for cross hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments.

Acid-proof dishes and tubes have been made out of tungsten; furthermore, tungsten wire recommends itself as a unit resistance, since it can be made absolutely pure, can be easily duplicated, and is not corroded.

Since tungsten is paramagnetic and elastic, it is being tried out in electrical meters, replacing the phosphor-bronze springs. Similarly watch springs could be made which would never become magnetised. Finally, tungsten pen points, tungsten drawing dies, tungsten knife blades, tungsten reinforced asbestos curtains, and fireproof coverings, &c., were mentioned.

Table of Physical and Chemical Properties of Ductile Tungsten.

Density, 19·3 to 20·2.

Tensile strength, 322 to 427 kilogrms. per square mm.

Young's modulus of elasticity, 42,200 kilogrms. per square mm. (steel 20,000).

Melting-point, 3177° C. (Langmuir); 3100° ± 60° C. (Pirani and Meyer).

Boiling-point, 3700° C.?

Thermal conductivity, 0·35 grm. cal. per cc. per second per 1° (Pt 0·166).

Expansion coefficient, $4{\cdot}3 \times 10^6$ (Pt $8{\cdot}8 \times 10^6$).

Specific heat, 0·0358 (Weiss).

Resistivity, hard: 6·2 microhms per cc., and annealed 5·0 microhms per c.c.

Temperature coefficient of resistance, 0·0051 (0—170°).

Magnetic susceptibility: $+0.33 \times 10^6$ (Honda); that is, practically nonmagnetic.

Hardness, 4·5 to 8 (Mobs scale).

Insoluble in HCl, H_2SO_4, HNO_3, HF, NaOH, KOH (aq), and mixtures of $K_2Cr_2O_7 + H_2SO_4$, soluble in mixtures of HF and HNO_3 and in fused nitrates and peroxides.

The boiling-point of the metal has not yet been determined.—*Mineral Resources of the United States*, 1913, *Part II., U.S. Geological Survey.*

NOTICES OF BOOKS.

Industrial Gases, including the Liquefaction of Gases. By Geoffrey Martin, D.Sc., Ph.D., F.C.S.; Ernest A. Dancaster, B.Sc.; J. M. Dickson, B.Sc.; Frank B. Gatehouse, F.C.S.; E. Jobling, A.R.C.Sc., B.Sc., F.C.S., and H. Stanley Redgrove, B.Sc., F.C.S. London: Crosby Lockwood and Son. 1916. Pp. viii.+150. Price 7s. 6d. net.

This manual deals with the liquefaction and manufacture of gases of technical importance, including hydrogen, oxygen, nitrogen, carbon dioxide, sulphur dioxide, ammonia, &c. Short accounts are given of the plant and processes employed for the individual gases, but in many cases the descriptions are too brief to be of much service to those who are not already well acquainted with the methods. Thus, in the case of oxygen, the accounts of the manufacture, properties, and uses occupy barely a page, and are really not much more than a few notes on the subject. References to other works for fuller information are frequent, though the lists of books and literature generally will be found useful. The ammonia and ammonium salts industry is treated rather more fully than other subjects, and this section will be found of considerable practical value. A fairly full account also is given in the last chapter of industrial ozone, and the various systems of preparation in use are described in some detail.

Aids to Bacteriology. By C. G. Moor, M.A. (Cantab.), F.I.C., and William Partridge, F.I.C. Third Edition. London: Baillière, Tindall, and Cox. 1916. Pp. viii.+278. Price 3s. 6d. net Cloth, 3s. net Paper.

The third edition of this little book contains a good deal of fresh matter and new references, some chapters having been very considerably extended. The investigation of questions arising from the occupation of highly cultivated land by very large numbers of troops has led to an increased knowledge of certain organisms, which is well summarised from the point of view of bacteriology, and more space is devoted to the meningococcus and to the discussion of the values and uses of different antiseptics. The work which has recently been done on filterable viruses is given in one chapter, and investigations of soil sterilisation and nitrogen fixation are also reviewed. Bacteriology is essentially a subject in which personal observation by practical work is the only possible way of acquiring knowledge, but that is not to say that a book such as this, giving the results of long experience, may not be a useful aid.

The Health of the Skin. By George Pernet, M.D. London: Methuen and Co., Ltd. 1916. Pp. vii.+103. Price 1s. net.

This little book contains a popular account of the anatomy and physiology of the skin, and discusses questions of general hygiene, clothing, the use of cosmetics, &c., in a pleasantly chatty style. There is plenty of good science and sound common sense in the advice given, and diseases of the skin and their cure are treated adequately for the purpose of the book. The hair and nails are included, and those who require a non-technical and readable guide in their search for health and strength will find it, as far as the skin, &c., is concerned, in this little manual.

Special Reports on the Mineral Resources of Great Britain. Volume V. *Potash Felspar, Phosphate of Lime, &c.* By A. Strahan, Sc.D., LL.D., F.R.S., J. S. Flett, D.Sc., LL.D., F.R.S., and C. H. Dinham, B.A. London: Printed under the Authority of His Majesty's Stationery Office by Jas. Truscott and Son, Ltd. 1916. Pp. 41. Price 1s.

This volume of the special reports of the mineral resources of Great Britain deals with potash felspar, phosphate of lime, alum shales, plumbago, molybdenite, chromite, talc and steatite, and diatomite, some of which have been worked in England, although for various reasons their production has now ceased. The chapters on potash felspar contain some accounts of the methods which have been suggested for the extraction of potash from it, and details are given of the distribution of pegmatite in Scotland and of the composition of the mineral. Phosphate of lime, alum shales, and the other minerals enumerated are treated similarly, in all cases notes being added upon the uses to which they have been put.

Manufacture of Gasoline and Benzene-Toluene from Petroleum and other Hydrocarbons. By W. F. Rittman, C. B. Dutton, and E. W. Dean. Washington: Government Printing Office. 1916. Pp. xvii.+268. Price 35 cents.

The Bureau of Mines has recently established at Pittsburgh, Pa., a laboratory in which problems connected with the economical use of petroleum are investigated, and it is hoped that the outcome of the work done there will be the saving of waste of the oil resources of the United States. The conversion of the heavier into the more useful lighter oils is an economical process of the highest importance, and this "cracking process" has been made the subject of a very thorough study by the workers in the laboratory, the results of which are given in this bulletin. The most favourable conditions for obtaining the maximum yields of the products were very carefully investigated both on a laboratory and on a large scale, and it was found that it is best to keep the hydrocarbon in a gaseous state throughout the entire process. The different factors affecting the cracking process were subjected to exhaustive study, and it was found that the gaseous phase process presents many advantages over the older methods.

Economic Methods of Utilising Western Lignites. By E. J. Babcock. Washington Government Printing Office. 1915. Pp. 73. Price 15 cents.

This bulletin, of which a limited free edition is issued by the Bureau of Mines, gives a summary of the results which have been obtained in the investigation of lignite carried out at the College of Mining Engineering at Grand Forks, North Dakota, and at the mining substation at Hebron. The special object of the work was the study of the production of gas from the vast deposits of lignite in the West Central and Western States, and the economical utilisation of the gas for power purposes and for domestic lighting and heating. The experimental tests were exceedingly numerous and were well planned and efficiently carried out. It was found that both for power and for domestic purposes it is most beneficial to break the lignite up into lumps of a small, uniform size, and that drying is also essential. The most economical way to use the lignite appears to be in the form of residue briquets and the manufacture of by-product gas, and it is claimed that the briquets approach anthracite in value. The author does not find it possible to give details of the cost of operating large commercial plants because local conditions cause such very great variations in the cost, but it is believed that a profitable industry could readily be developed which would be of very great value to the towns and villages in the Western States.

THE CHEMICAL NEWS.

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ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.

Newcastle-on-Tyne, 1916.

By Prof. G. G. HENDERSON, D.Sc., LL.D., F.R.S.,
President of the Section.

For the third time in succession the Section meets under the shadow of the war cloud, but there is some slight consolation for the indescribable suffering and sorrow which have been imposed upon millions of our fellow creatures in the hope and belief that this cloud also may have a silver lining. It is perhaps no exaggeration to say that nothing less than such an upheaval of existing habits and traditions as has been caused by the war would have sufficed to arouse the British nation from the state of apathy towards science with which it has been fatuously contented in the past. Now, however, the sleeper has at least stirred in his slumber. The Press bears witness, through the appearance of innumerable articles and letters, that the people of this country, and even the politicians, have begun to perceive the dangers which will inevitably result from a continuance of their former attitude, and to understand that in peace, as in war, civilisation is at a tremendous disadvantage in the struggle for existence unless armed by science, and that the future prosperity of the Empire is ultimately dependent upon the progress of science, and very specially of chemistry. If, as one result of the war, our people are led to appreciate the value of scientific work, then perhaps we shall not have paid too high a price, high although the price must be. As concerns our own branch of science, we cannot rest satisfied with anything less than full recognition of the fact that chemistry is a profession of fundamental importance, and that the chemist is entitled to a position in no respect inferior to that of a member of any of the other learned professions.

Reference to the Annual Reports of the Association shows that former Presidents of the Section have availed themselves to the full of the latitude permitted in the choice of a subject for their Address, and that some have even established the precedent of dispensing with an Address altogether. On the present occasion a topic for discussion seems to be clearly indicated by the circumstances in which we stand, because, since the outbreak of the war, chemists have been giving more earnest consideration than before to the present position and future prospects of the chemical industry of this country. It will therefore not be inappropriate if I touch upon some aspects of this question, even although unable to add much to what is, or ought to be, common knowledge.

The period which has elapsed since the last meeting of the Section in Newcastle has witnessed truly remarkable progress in every branch of pure and applied chemistry. For fully fifty years previous to that meeting the attention of the great majority of chemists had been devoted to organic chemistry, but since 1885 or thereabouts, whilst the study of the compounds of carbon has been pursued with unflagging energy and success, it has no longer so largely monopolised the activities of investigators. Interest in the other elements, which had been to some extent neglected on account of the fascinations of carbon, has been revived with the happiest results, for not only has our knowledge of these elements been greatly extended, but their number also has been notably increased by the discovery of two groups of simple substances possessed of new and remarkable properties—the inert gases of the argon family and the radio-active elements. In addition, the bonds between mathematics and physics on the one hand and chemistry on the other have been drawn closer, with the effect that the department of our science known as physical chemistry has now assumed a position of first-rate importance. With the additional light provided by the development and application of physico-chemical theory and methods we are beginning to gain some insight into such intricate problems as the relation between physical properties and chemical constitution, the structure of molecules and even of atoms, and the mechanics of chemical change; our outlook is being widened and our conceptions rendered more precise. Striking advances have also been made in other directions. The extremely difficult problems which confront the bio-chemist are being gradually overcome, thanks to the indefatigable labours of a band of highly skilled observers, and the department of biological chemistry has been established on a firm footing through the encouraging results obtained within the period under review. Further, within the last few years many of our ideas have been subjected to a revolutionary change through the study of the radio-active elements, these elusive substances which occur in such tantalisingly minute quantities, and of which some appear so reluctant to exist in a free and independent state that they merge their identity in that of another and less retiring relative within an interval of time measured by seconds. In truth, if a Rip Van Winkle among chemists were to awake now after a slumber of thirty years his amazement on coming into contact with the chemistry of to-day would be beyond words.

The more purely scientific side of our science can claim no monopoly in progress, for applied chemistry in every department has likewise advanced with giant strides, mainly of course through the application of the results of scientific research to industrial purposes. An attempt to sketch in the merest outline the recent development of applied chemistry would I fear exhaust your patience, but I may indicate in passing some of the main lines of advance. Many of the more striking results in the field of modern chemical industry have been obtained by taking advantage of the powers we now possess to carry out operations economically both at very high and at very low temperatures, and by the employment on the manufacturing scale of electrolytic and catalytic methods of production. Thanks largely to the invention of the dynamo, the technologist is now able to utilise electrical energy both for the production of high temperatures in the different types of electric furnace and for electrolytic processes of the most varied description. Among the operations carried out with the help of the electric furnace may be mentioned the manufacture of graphite, silicon, and phosphorus; of chromium and other metals; of carbides, silicides, and nitrides; and the smelting and refining of iron and steel. Calcium carbide claims a prominent place in the list, in the first place because of the ease with which it yields acetylene, which is not only used as an illuminant, and, in the oxy-acetylene burner, as a means of producing a temperature so high that the cutting and welding of steel is now a comparatively simple matter, but also promises to serve as the starting-point for the industrial synthesis of acetaldehyde and many other valuable organic compounds. Moreover, calcium carbide is readily converted in the electric furnace into calcium cyanamide, which is employed as an efficient fertiliser in place of sodium nitrate or ammonium sulphate, and as a source of ammonia and of alkali cyanides. Among the silicides carborundum is increasingly used as an abrasive and a refractory material, and calcium silicide, which is now a commercial product, forms a constituent of some blasting explosives. The Serpek process for the preparation of alumina and ammonia by the formation of aluminium nitride from bauxite in the electric furnace and its subsequent decomposition by caustic soda should also be mentioned. Further, the electric furnace has made possible the manufacture of silica apparatus of all kinds, both for the laboratory and the works, and of alundum ware, also used for operations at high temperature. Finally, the first step in the manufacture of nitric acid and of nitrites from air, now in operation on a very large scale, is the combustion of nitrogen in the electric arc.

In other industrial operations the high temperature which is necesssary is obtained by the help of the oxy-hydrogen or the oxy-acetylene flame, the former being used, amongst other purposes, in a small but I believe profitable industry, the manufacture of synthetic rubies, sapphires, and spinels. Also, within a comparatively recent period, advantage has been taken of the characteristic properties of aluminium, now obtainable at a moderate price, in the various operations classed under the heading alumino-thermy, the most important being the reduction of refractory metallic oxides, although, of course, thermite is useful for the production of high temperatures locally.

The modern methods of liquefying gases, which have been developed within the period under review, have rendered possible research work of absorbing interest on the effect of very low temperatures on the properties and chemical activity of many substances, and have been applied, for instance, in separating from one another the members of the argon family, and in obtaining ozone in a state of practical purity. Moreover, industrial applications of these methods are not lacking, amongst which I may mention the separation of nitrogen and oxygen from air, and of hydrogen from water-gas—processes which have helped to make these elements available for economic use on the large scale.

Electrolytic methods are now extensively employed in the manufacture of both inorganic and organic substances, and older processes are being displaced by these modern rivals in steadily increasing number. It is sufficient to refer to the preparation of sodium, magnesium, calcium, and aluminium by electrolysis of fused compounds of these metals; the refining of iron, copper, silver, and gold; the extraction of gold and nickel from solution; the recovery of tin from waste tin-plate; the preparation of caustic alkalis (and simultaneously of chlorine), of hypochlorites, chlorates, and perchlorates, of hydrosulphites, of permanganates and ferricyanides, of persulphates and percarbonates; the regeneration of chromic acid from chromium salts; the preparation of hydrogen and oxygen. As regards organic compounds, we find chiefly in use electrolytic methods of reduction, which are specially effective in the case of many nitro compounds, and of oxidation, as for instance the conversion of anthracene into anthraquinone. At the same time a number of other compounds, for example iodoform, are also prepared electrolytically.

Within recent years there have been great advances in the application of catalytic methods to industrial purposes. Some processes of this class have, of course, been in use for a considerable time, for example the Deacon chlorine process and the contact method for the manufacture of sulphuric acid, whilst the preparation of phthalic anhydride (largely used in the synthesis of indigo and other dyestuffs), by the oxidation of naphthalene with sulphuric acid with the assistance of mercuric sulphate as catalyst, is no novelty. More recent are the contact methods of obtaining ammonia by the direct combination of nitrogen and hydrogen, and of oxidising ammonia to nitric acid—both of which are said to be in operation on a very large scale in Germany. The catalytic action of metals, particularly nickel and copper, is utilised in processes of hydrogenation—for example, the hardening of fats, and of dehydrogenation, as in the preparation of acetaldehyde from alcohol, and such metallic oxides as alumina and thoria can be used for processes of dehydration—*e.g.*, the preparation of ethylene or of ether from alcohol. Other catalysts employed in industrial processes are titanous chloride in electrolytic reductions and cerous sulphate in electrolytic oxidations of carbon compounds, gelatin in the preparation of hydrazine from ammonium, sodium in the synthesis of rubber, &c.

Other advances in manufacturing chemistry include the preparation of a number of the rarer elements and their compounds, which were hardly known thirty years ago, but which now find commercial applications. Included in this category are titanium, vanadium, tungsten, and tantalum, now used in metallurgy or for electric-lamp filaments; thoria and ceria in the form of mantles for incandescent lamps; pyrophoric alloys of cerium and other metals; zirconia, which appears to be a most valuable refractory material; and compounds of radium and mesothorium, for medical use as well as for research. Hydrogen, together with oxygen and nitrogen, are in demand for synthetic purposes, and the first also for lighter-than-air craft. Ozone is considerably used for sterilising water and as an oxidising agent, for example in the preparation of vanillin from isoeugenol, and hydrogen peroxide, now obtainable very pure in concentrated solution, and the peroxides of a number of the metals are also utilised in many different ways. The per- acids—perboric, percarbonic, and persulphuric—or their salts are employed for oxidising and bleaching purposes, and sodium hydrosulphite is much in demand as a reducing agent—*e.g.* in dyeing with indigo. Hydroxylamine and hydrazine are used in considerable quantity, and the manufacture of cyanides by one or other of the modern methods has become quite an important industry, mainly owing to the use of the alkali salts in the cyanide process of gold extraction. These remarkable compounds the metallic carbonyls have been investigated, and nickel carbonyl is employed on the commercial scale in the extraction of the metal. Fine chemicals for analysis and research are now supplied, as a matter of course, in a state of purity rarely attained a quarter of a century ago.

In the organic chemical industry similar continued progress is to be noted. Accessions are constantly being made to the already enormous list of synthetic dyes, not only by the addition of new members to existing groups, but also by the discovery of entirely new classes of tinctorial compounds; natural indigo seems doomed to share the fate of alizarine from madder, and to be ousted by synthetic indigo, of which, moreover, a number of useful derivatives are also made. Synthetic drugs of all kinds—antipyrine and phenacetin, sulphonal and veronal, novacain and β-eucaine, salol and aspirin, piperazine and adrenaline, atoxyl and salvarsan—are produced in large quantities, as also are many synthetic perfumes and flavouring materials, such as ionone, heliotropine, and vanillin. Cellulose in the form of artificial silk is much used as a new textile material, synthetic camphor is on the market, synthetic rubber is said to be produced in considerable quantity; and the manufacture of materials for photographic work and of organic compounds for research purposes is no small part of the industry. However, it would serve no useful purpose to extend this catalogue, which might be done almost indefinitely. British chemists are entitled to regard with satisfaction the part which they have taken in the development of scientific chemistry during the last three decades, as in the past, but with respect to the progress of industrial chemistry it must be regretfully admitted that, except in isolated cases, we have failed to keep pace with our competitors. Consider a single example. Although there still remain in South America considerable deposits of sodium nitrate which can be worked at a profit, it is clear that sooner or later other sources of nitric acid must be made available. The synthetic production of nitric acid from the air is now a commercial success; several different processes are in operation abroad, and Germany is reported to be quite independent of outside supplies. Electrical energy, upon the cost of which the success of the process largely depends, can be produced in this country at least as cheaply as in Germany, and yet we have done nothing in the matter, unless we count as something the appointment of a committee to consider possibilities. This case is only too typical of many others.

A number of different causes have contributed to bring about this state of affairs, and the responsibility for it is assigned by some to the Government, by others to the chemical manufacturers, and by still others to the professors of chemistry. I think, however, it will be generally admitted that the root of the matter is to be found in the general ignorance of and indifference to the methods and results of scientific work which characterises the people of this country. For many years past our leaders in science have done all that lay in their power to awaken the country to the inevitable and deplorable results of this form of "sleeping sickness," but hitherto their reception has been much the same as that accorded to the hero of "The Pilgrim's Progress," as depicted in the following passage :—

"He went on thus, even until he came at a bottom where he saw, a little out of the way, three Men fast asleep with Fetters upon their heels.

"The name of the one was *Simple*, another *Sloth*, and the third *Presumption*.

"Christian, then seeing them in this case, went to them, if peradventure he might awaken them. And cried, You are like them that sleep on the top of a Mast, for the Dead Sea is under you, a Gulf that hath no bottom. Awake therefore and come away; be willing also, and I will help you off with your irons. He also told them, If he that goeth about like a *Roaring Lion* comes by, you will certainly become a prey to his teeth.

"With that they lookt upon him, and began to reply in this sort: *Simple* said, *I see no danger ; Sloth* said, *Yet a little more sleep* ; and *Presumption* said, *Every vat must stand upon his own bottom*. And they lay down to sleep again, and *Christian* went on his way."

I believe that a brighter day is dawning, and that, if only we rise to the occasion *now*, chemistry in this country will attain the position of importance which is its due. Meantime it is of no avail to lament lost opportunities or to indulge in unprofitable recrimination ; on the contrary, it should be our business to find a remedy for the "arrested development" of our chemical industry, and the task of establishing remedial measures should be taken in hand by the State, the universities, and the chemical manufacturers themselves. As regards another very large group of interested persons, the consumers of chemical products, or in other words the nation as a whole, it is surely not too much to expect that they have been taught by the course of events since the outbreak of the war the folly of depending solely upon foreign and possibly hostile manufacturers, even although fiscal and other advantages may enable the alien to undersell the home producer. Considering that the future prosperity of the Empire depends largely upon the well-being of its chemical industries, it is simply suicidal to permit these to be crippled or even crushed out of existence by competition on unequal terms.

The Government has taken a most significant step in advance by appointing an Advisory Council for Scientific and Industrial Research and providing it with funds ; incidentally, in so doing, it has recognised the past failure of the State to afford adequate support to scientific work. The Advisory Council has lost no time in getting to work and has already taken steps to allocate grants in support of a number of investigations of first-rate importance to industry. In order to be in a position to do justice to the branches of industry concerned in proposed researches which have been submitted by institutions and individuals it has decided to appoint standing committees of experts and has already constituted strong Committees in Mining, Metallurgy, and in Engineering; a Committee in Chemistry will no doubt be appointed in due course. The Council also makes the gratifying intimation that the training of an adequate supply of research workers will be an important part of its work.

It is safe to prophesy that the money expended by the Advisory Council will sooner or later yield a goodly return, and this justifies the hope that the Government will not rest satisfied with their achievement, but will take further steps in the same direction. This desire for continued action finds strong support in the Recommendations made by a Sub-Committee of the Advisory Committee to the Board of Trade on Commercial Intelligence, which was appointed to report with respect to measures for securing the position, after the war, of certain branches of British industry. Of these recommendations I quote the following :—

"1. *Scientific Industrial Research and Training*.—(*a*) Larger funds should be placed at the disposal of the new Committee of the Privy Council, and also of the Board of Education, for the promotion of scientific and Industrial training. (*b*) The universities should be encouraged to maintain and extend research work devoted to the main industry or industries located in their respective districts, and manufacturers engaged in these industries should be encouraged to co-operate with the universities in such work, either through their existing trade associations or through associations specially formed for the purpose. Such associations should bring to the knowledge of the universities the difficulties and needs of the industries, and give financial and other assistance in addition to that afforded by the State. In the case of non-localised industries trade associations should be advised to seek, in respect of centres for research, the guidance of the Advisory Committee of the Privy Council. (*c*) An authoritative record of consultant scientists, chemists and engineers, and of persons engaged in industrial research, should be established and maintained by some suitable Government Department for the use of manufacturers only."

"2. *Tariff Protection*.—Where the national supply of certain manufactured articles which are of vital importance to the national safety or are essential to other industries has fallen into the hands of manufacturers or traders outside this country, British manufacturers ready to undertake the manufacture of such articles in this country should be afforded sufficient tariff protection to enable them to maintain such production after the war." (It is also recommended by the Sub-Committee that in view of the threatened dumping of stocks which may be accumulated in enemy countries, the Government should take such steps as would prevent the position of industries, likely to be affected, being endangered after the war).

"3. *Patents*.—(*a*) The efforts which have been made to secure uniformity of Patent Law throughout the Empire should be continued. (*b*) The provisions of the law as to the compulsory working of patents in the United Kingdom should be more rigorously enforced, and inspectors should be appointed to secure that such working is complete and not only partial."

The adoption by the Government of these weighty recomendations would go far to establish British chemical industry on a secure basis, and would undoubtedly lead to the expansion of already existing branches and the establishment of new ones. Meanwhile the Australian Government has set an example which might be followed with great advantage. Shortly after the British scheme for the development of scientific and industrial research under the auspices of the Advisory Council had been made public, the Prime Minister of Australia determined to do still more for the Commonwealth, with the object of making it independent of German trade and manufactures after the conclusion of the war. He therefore appointed a committee representative of the State Scientific Departments, the universities, and industrial interests, and within a very short period the committee produced a scheme for the establishment of a Commonwealth Institute of Science and Industry. The Institute is to be governed by three directors, two of whom will be scientific men of high standing, while the third will be selected for proved ability in business. The directors are to be assisted by an Advisory Council composed of nine representatives of science and of industry ; these representatives are to seek information, advice, and assistance from specialists throughou

Australia. The chief functions of the Institute are (1) To ascertain what industrial problems are most pressing and most likely to yield to scientific experimental investigation, to seek out the most competent men to whom such research may be entrusted, and to provide them with all the necessary appliances and assistance. (2) To build up a bureau of scientific and industrial information, which shall be at the service of all concerned in the industries and manufactures of the Commonwealth. (3) To erect, staff, and control special research laboratories, the first of which will probably be a physical laboratory somewhat on the lines of our National Physical Laboratory. Other functions of the Institute are the co-ordination and direction of research and experimental work with a view to the prevention of undesirable overlapping of effort, the recommendation of grants of the Commonwealth Government in aid of pure scientific research in existing institutions, and the establishment and award of industrial research fellowships.

This admirable scheme is more comprehensive and more generous than that of our Government, but it could be rivalled without much difficulty. We already possess an important asset in the National Physical Laboratory, and there now exists the Advisory Council with its extensive powers and duties. What is lacking in our scheme, so far as chemistry is concerned, could be made good, firstly, by providing the Advisory Council with much larger funds, and, secondly, by the establishment of a National Chemical Laboratory—an institute for research in pure and applied chemistry—or by assisting the development of research departments in our universities and technical colleges (as is now being done in America), or, better still, by moving in both directions. With respect to the second alternative, I do not mean to suggest that research work is neglected in the chemistry departments of any of our higher institutions; what I plead for is the provision of greater facilities for the prosecution of investigation not only in pure but also in applied chemistry. As things are at present, the professors and lecturers are for the most part so much occupied in teaching and in administration as to be unable to devote time uninterruptedly to research work, which demands above all things continuity of effort. The ideal remedy would be the institution of research professorships, but, failing this, the burden of teaching and administrative work should be lightened by appointing larger staffs.

It has been suggested by Dr. Forster that the State could render assistance to chemical industry in another way, namely, by the formation of a Chemical Intelligence Department of the Board of Trade, which should be concerned with technical, commercial, and educational questions bearing upon the industry. Under the first head the proposed Department would have the duty (*a*) of collecting, tabulating, and distributing all possible information regarding chemical discoveries, patents, and manufacturing processes, and (*b*) of presenting problems for investigation to research chemists, of course under proper safeguards and with suitable remuneration. The more strictly commercial side of the Department's activities would be concerned with the classification of the resources of the Empire as regards raw materials, and of foreign chemical products in respect of distribution throughout the world, with ruling prices, tariffs, cost of transport, and if possible cost of production. On the educational side it is suggested that the Department should collect data regarding opportunities for chemical instruction and research in various parts of the Empire, and should consider possible improvements and extensions of these. The Department would of course be in charge of a highly trained chemist, with a sufficient number of chemical assistants.

This proposal, which has been widely discussed and on the whole very favourably received by chemists, has much to recommend it; to mention only one point, the unrivalled resources of the Board of Trade would facilitate the acquisition of information which might otherwise be difficult to obtain, or which would not be disclosed except to a Government Department. The principal objections which have been raised are based upon the fear that the proposed Department, however energetic and enterprising it might be at the start, would soon be so helplessly gagged and bound down by departmental red tape as to become of little or no service. This danger, however, could be obviated to a great extent by the institution of a strong Advisory Committee, representative of and elected by the Societies concerned with the different branches of chemistry, which would keep closely in touch with the Chemical Intelligence Department on the one hand and with the industry on the other, and which would act as adviser of the permanent scientific staff of the Department. There is, I fear, little chance of seeing Dr. Forster's proposal carried into effect unless all the Societies concerned move actively and unitedly in the matter; they must do the pioneer work and must submit a definite scheme to the Government, if the desired result is to be attained. In the not improbable contingency that the Board of Trade will decline to take action, I trust that the scheme for the establishment of an Information Bureau—on lines similar to but somewhat less wide-reaching than those which I have just indicated—which has been under the careful consideration of the Council of the Society of Chemical Industry, will be vigorously prosecuted. Difficulties, chiefly financial, stand in the way, but these are not insuperable, especially if the sympathy and support of the Government can be enlisted.

Unless the conditions and methods which have ruled in the past are greatly altered it is hardly possible to hope that the future prospects of our chemical industry will be bright; it is essential that the representatives of the industry should organise themselves in their own interest and co-operate in fighting the common enemy. More than ever is this the case when, as we are informed, three different groups of German producers of dyes, drugs, and fine chemicals, who own seven large factories, have formed a combination, with a capital of more than £11,000,000, and with other assets of very great value in the shape of scientific, technical, and financial efficiency. Hence it is eminently satisfactory to be able to record the active progress of a movement, originated by the Chemical Society, which has culminated in the formation of an Association of British Chemical Manufacturers. The main objects of the Association are to promote co-operation between British chemical manufacturers; to act as a medium for placing before the Government and Government officials the views of manufacturers upon matters affecting the chemical industry; to develop technical organisation and promote industrial research; to keep in touch with the progress of chemical knowledge and to facilitate the development of new British industries and the extension of existing ones; and to encourage the sympathetic association of British manufacturers with the various universities and technical colleges.

Needless to say, the progress of this important movement will be assisted by everyone who is interested, either directly or indirectly, in the welfare of our chemical industry, and, moreover, the support of the scientific societies will not be lacking, for, as the result of a conference convened by the President and Council of the Royal Society, a Conjoint Board of Scientific Societies has been constituted, for the furtherance of the following objects:—Promoting the co-operation of those interested in pure or applied science; supplying a means whereby scientific opinion may find effective expression on matters relating to science, industry, and education; taking such action as may be necessary to promote the application of science to our industries and to the service of the nation; and discussing scientific questions in which international co-operation seems advisable.

In an Address given to the Society of Chemical Industry last year, I indicated another way in which chemical manufacturers can help themselves and at the same time promote the interests of chemistry in this country. In the

United States of America individual manufacturers, or associations of manufacturers, have shown themselves ready to take up the scheme originated by the late Professor Duncan for the institution of industrial research scholarships tenable at the universities or technical colleges, and the results obtained after ten years' experience of the working of this practical method of promoting co-operation between science and industry have more than justified the anticipations of its originator. The scheme is worthy of adoption on many grounds, of which the chief are that it provides definite subjects for technical research to young chemists qualified for such work, that it usually leads to positions in factories for chemists who have proved their capacity through the work done while holding scholarships, and that it reacts for good on the profession generally, by bringing about that more intimate intercourse between teachers and manufacturers which is so much to be desired.

In this connection the recent foundation of the Willard Gibbs Chair of research in pure chemistry at the University of Pittsburgh is extremely significant, for it shows that even in such a purely industrial community as Pittsburgh it is recognised that the most pressing need of the day is the endowment of chemical research and the creation of research professorships. Mr. A. P. Fleming, who recently made a tour of inspection of research laboratories in the United States, points to the amount of work done by individual firms and the increased provision now being made for research in universities and technical institutions. He reports that at the present time there are upwards of fifty corporations having research laboratories, costing annually from £20,000 to £100,000 for maintenance, and states that "some of the most striking features of the research work in America are the lavish manner in which the laboratories have been planned, which in many cases enables large scale operations to be carried out in order to determine the best possible methods of manufacturing any commodity developed or discovered in the laboratories; the increasing attention given in the research laboratories to pure science investigation, this being, in my opinion, the most important phase of industrial research; and the absorption of men who have proven their capacity for industrial research in such places as the Mellon Institute, the Bureau of Standards, &c., by the various industries in which they have taken scientific interest." It is evidently the view of American manufacturers that industrial research can be made to pay for itself, and that to equip and maintain research laboratories is an excellent investment.

It cannot be too often reiterated that no branch of chemical industry can afford to stand still, for there is no finality in manufacturing processes; all are capable or improvement, and for this, as well as for the discovery and the application of new processes, the services of the trained chemist are essential. Hence the training of chemists for industrial work is a matter of supreme importance. We may therefore congratulate ourselves that the opportunities for chemical instruction in this country are immensely greater than they were thirty years ago. The claims of chemistry to a leading position have been recognised by all our universities, even the most ancient, by the provision of teaching staffs, laboratories, and equipment on a fairly adequate if not a lavish scale, and in this respect many of the technical colleges fall not far behind. The evening classes conducted in a large number of technical institutions are hardly fitted to produce fully trained chemists, if only because lack of the necessary time prevents the student from obtaining that prolonged practice in the laboratory which cannot be dispensed with, unless indeed he is prepared to go through a course of study extending over many years. At the same time these evening classes play a most important part, firstly in disseminating a knowledge of chemistry throughout the country, and secondly in affording instruction of a high order in special branches of applied chemistry. Finally, in a large and increasing number of schools a more or less satisfactory introduction to the science is given by well-qualified teachers. With our national habit of self-depreciation we are apt to overlook the steady progress which has been made, but at the same time I do not suggest that there is no room for improvement of our system of training chemists. Progress in every department of industrial chemistry is ultimately dependent upon research, and therefore a sufficient supply of chemists with practical knowledge and experience of the methods of research is vital. This being so, it is an unfortunate thing that so many students are allowed to leave the universities in possession of a science degree but without any experience in investigation. The training of the chemist, so far as that training can be given in a teaching institution, must be regarded as incomplete unless it includes some research work, not, of course, because every student has the mental gifts which characterise the born investigator, but rather because of the inestimable value of the experience gained when he has to leave the beaten track and to place more dependence upon his own initiative and resource. Consequently one rejoices to learn that at the University of Oxford no candidate can now obtain an Honours degree without having produced evidence that he has taken part in original research, and that the General Board of Studies at Cambridge has also made proposals which, if adopted, will have the effect of encouraging systematic research work. Perhaps it is too much to expect that practice in research will be made an indispensable qualification for the ordinary degree; failing this, and indeed in every case, promising students should be encouraged, by the award of research scholarships, to continue their studies for a period of at least two years after taking the B.Sc. degree, and to devote that time to research work which would qualify for a higher degree. In this connection an excellent object-lesson is at hand, for the output of research work from the Scottish Universities has very greatly increased since the scheme of the Carnegie Trust for the institution of research scholarships has come into operation. Thanks to these scholarships, numbers of capable young graduates, who otherwise for the most part would have had to seek paid employment as soon as their degree courses were completed, have been enabled to devote two or more years to research work. Of course it must be recognised that not every chemist has the capacity to initiate or inspire investigation, and that no amount of training, however thorough and comprehensive, will make a man an investigator unless he has the natural gift. At the same time, whilst only the few are able to originate really valuable research work, a large army of disciplined men who have had training in the methods of research is required to carry out experimentally the ideas of the master mind. Moreover, there is ample scope in industrial work for chemists who, although not gifted with initiative as investigators, are suitably equipped to supervise and control the running of large-scale processes, the designing of appropriate plant, the working out on the manufacturing scale of new processes or the improvement of existing ones—men of a thoroughly practical mind, who never lose sight of costs, output, and efficiency, and who have a sufficient knowledge of engineering to make their ideas and suggestions clear to the engineering expert. Further, there has to be considered the necessity for the work of the skilled analyst in the examination of raw materials and the testing of intermediate and finished products, although much of the routine work of the industrial laboratory will advisedly be left in the hands of apprentices working under the control of the chemist. Lastly, for the buying and selling of materials there should be a demand for the chemist with the commercial faculty highly developed. There is, indeed, in any large industrial establishment room for chemists of several different types, but all of these should have had the best possible training, and it must be the business of our higher teaching institutions to see that this training is provided.

On more than one occasion I have expressed the opinion that every chemist who looks forward to an industrial post should receive in the course of his training a certain amount of instruction in chemical engineering, by means of lectures and also of practical work in laboratories fitted out for the purpose. The practicability of this has been proved in more than one teaching institution, and experience has convinced me that chemists who have had such a course are generally more valuable in a works—whether their ultimate destination is the industrial research laboratory or the control of manufacturing operations—than those who have not had their studies directed beyond the traditional boundaries of pure chemistry. (I used the word "traditional" because to my mind there is no boundary line between the domains of pure and of applied chemistry). A course in chemical engineering, preferably preceded by a short course in general engineering and drawing, must, however, be introduced as *a supplement to*, and not as a *a substitute for*, any part of the necessary work in pure chemistry, and consequently the period of undergraduate study will be lengthened if such a course is included; this is no disadvantage, but quite the contrary. I am glad to say that the University of Glasgow has recently instituted a degree in Applied Chemistry, for which the curriculum includes chemical engineering in addition to the usual courses in chemistry, and I hope that a place will be found for this subject by other universities.

On the whole, there is not much fault to be found with the training for chemists supplied by the universities and technical colleges, but there is still room for improvements which could and would be carried out if it were not that the scientific departments of these institutions are as a rule hampered by lack of funds. The facilities for practical instruction with respect to accommodation and equipment are generally adequate, but on the other hand, the *personnel* could with advantage be largely increased, and at least the junior members of the staffs are miserably underpaid. It would doubtless be regarded as insanity to suggest that a scientific man, however eminent, should receive more than a fraction of the salary to which a music-hall "artiste" or a lawyer politician can aspire; but if the best brains in the country are to be attracted towards science, as they ought to be, some greater inducement than a mere living wage should be held out. Hence no opportunity should be lost of impressing upon the Government the necessity for increasing the grants to the scientific departments of our higher teaching institutions, and for the provision of research scholarships. It is much to be desired also that wealthy men in this country should take an example from America and acquire more generally the habit of devoting some part of their means to the endowment of higher education. The private donations for science and education made in the United States during the last forty-three years amount to the magnificent sum of £117,000,000, and recently the average annual benefactions for educational purposes total nearly £6,000,000. Of course there are few, if any, of the universities and colleges in this country which are not deeply indebted to the foresight and generosity of private benefactors, but the lavish scale on which funds are provided in America leads to a certain feeling of admiring envy.

After all, the chief difficulty which confronts those who are eager for progress in educational matters is that so many of our most famous schools are still conducted on mediæval lines, in the sense that the "education" administered is almost wholly classical. Consequently, "though science enters into every part of modern life, and scientific method is necessary for success in all undertakings, the affairs of the country are in the hands of legislators who not only have little or no acquaintance with the fundamental facts and principles signified by these aspects of knowledge, but also do not understand how such matters can be used to strengthen and develop the State. Our administrative officials are also mostly under the same disabilities, on account of their want of a scientific training. They are educated at schools where science can receive little encouragement, and they do not take up scientific subjects in the examinations for the Civil Service, because marks can be much more easily obtained by attention to Latin and Greek; and the result of it all is that science is usually treated with indifference, often with contempt, and rarely with intelligent appreciation by the statesmen and members of the public services whose decisions and acts largely determine the country's welfare. The defects of a system which places the chief power of an organisation which needs understanding of science in every department in the hands of people who have not received any training in scientific subjects or methods are obvious."—(*Nature*, Feb. 10, 1916). The remedy is also obvious.

Here, again, the prospects are now brighter than ever before, because the warnings and appeals of men of science have at last, and after many years, begun to bear fruit, or perhaps it would be more correct to say the lessons of the war have begun to make an impression on the powers that be. Within the last few weeks it has been intimated that the Government, giving ear to what has been uttered, incessantly and almost *ad nauseam*, with regard to British neglect of science, propose to appoint a committee to inquire into the position of science in our national system of education, especially in universities and secondary schools. The duty of the committee will be to advise the authorities how to promote the advancement of pure science, and also the interests of trade, industries, and professions dependent on the application of science, bearing in mind the needs of what is described as a liberal education. It is stated that the committee will include scientific men in whom the country will have confidence, some of those who appreciate the application of science to commerce and industry, and some who are able from general experience to correlate scientific teaching with education as a whole. I am sure that we may look forward with confidence to the recommendations of such a committee, and we shall hope, for the sake of our country, that their recommendations will be adopted and put in force with the least possible delay.

THE CONSTITUTION OF COAL.[*]

By DAVID TREVOR JONES, M.Sc.,
and
RICHARD VERNON WHEELER, D.Sc.

Coal is considered to have been formed from decayed vegetable matter by the action of pressure and temperature. The temperature must have fallen short of 300° C.

The coal conglomerate can be resolved by means of solvents into cellulosic and resinic portions. The cellulosic derivatives contain compounds the molecules of which possess the furan structure, and yield phenols when destructively distilled. There are also compounds present the molecules of which have structures resembling that of the carbon molecule, but it is unlikely that "free" carbon is present in coal. The cellulosic derivatives are probably few in type. The resinic derivatives contain compounds in which alkyl, naphthene, and unsaturated hydroaromatic radicles are attached to larger and more complex groupings. It is doubtful whether aromatic groupings are present. Under the influence of pressure the bulk of the resinic derivatives have become highly polymerised. The oxygenated resinic derivatives are chiefly oxides, probably cyclic oxides; esters, lactones, anhydrides, acids, and ketones are absent or present only in small quantity. Hydrocarbons exist in the resinic portion of coal; saturated hydrocarbons (paraffins) are, however, present in small quantities only.

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[*] Read before the British Association (Section B), Newcastle Meeting, 1916.

DYNAMIC ISOMERISM.[*]

IMPORTANT new evidence, which has been accumulating during the past year, indicates even more clearly than before that liquids containing a single optically active component, of definite composition, and of fixed molecular structure, may be expected in the majority of cases to exhibit the "simple" type of rotary dispersion expressed by the formula $\alpha \lambda^2 - \lambda_0^2) = \text{const.}$ This formula has been tested in the case of forty-two compounds of the terpene series, for which data has recently been supplied by Prof. Rupe, of Basel (*Ann.*, 1914, cdix., 327), with the remarkable result that all but three have been found to conform closely to the "simple" dispersion law. In view of the complicated character of the molecular structure in these compounds (which contain one, two, or three asymmetric carbon atoms, complex ring systems, and unsaturated linkages), it is clear that "simple" rotary dispersion is not dependent on simple molecular structure, provided that the active substance is strictly homogeneous. "Complex" or "anomalous" rotatory dispersion in an optically-active liquid (and especially in a liquid of apparently simple character) may therefore be regarded as an *à priori* reason for suspecting the existence of some anomaly of chemical composition—*e.g.*, polymerism, association or dissociation, or dynamic isomerism.

THE OCCURRENCE OF GERMANIUM IN ZINC MATERIALS.

By G. H. BUCHANAN.

IN a recent issue of the journal (*Journ. Ind. Eng. Chem.*, 1916, viii., 225) W. F. Hillebrand and J. A. Scherrer contribute a short article on "The Recovery of Gallium from Spelter in the United States." In addition to the observations on gallium mention is made of the fact that Dr. K. Burns, of the Bureau of Standards, has examined spectroscopically several samples of zinc ore from various sources, and has identified in several of them, notably in a Missouri sulphide, the very rare element germanium. These observations concerning germanium are of particular interest to us, since in recent work we also have encountered this element in a by-product derived from Wisconsin blende. The exact nature of this by-product it is not possible to disclose at present.

The occurrence of germanium in blendes has been noted by Urbain (*Comptes Rendus*, cxlix., 602; cl., 1758). By spectroscopic methods this investigator detected germanium in thirty-eight out of eighty-four blendes from various localities. From 550 kilogrms. of one of the richest of these, a Mexican blende, he obtained 5 grms. of pure germanium. The amounts of the element found have always been small, the aid of the spectroscope being usually required to establish the identification. In the material at our disposal, however, germanium was found in sufficient quantity to be readily detected by the ordinary chemical reagents.

The presence of an unusual element had been indicated in the course of analysis, and further investigation showed that this was some member of the tin sub-group of the hydrogen sulphide group. The materials were therefore examined for the less common elements of this group. By the experiments briefly outlined in the succeeding paragraphs we convinced ourselves that we were dealing with an altogether unsuspected constituent, the element germanium, and that it was present in considerable amount.

Several 100-grm. portions of the substance were treated with concentrated hydrochloric acid, and the resulting solutions were distilled to about one-half volume, a current of chlorine being passed through the boiling mixture to maintain the arsenic in the pentavalent form. The distillate contained the unknown element.

On dilution of the distillate with a small amount of water and treatment with hydrogen sulphide a white flocculent precipitate was formed. If, however, the distillate was greatly diluted with water such precipitation took place but slowly and incompletely; the addition of strong hydrochloric acid to such solutions caused immediate precipitation. A considerable excess of strong acid was always found necessary for rapid precipitation of the sulphide.

The white sulphide, precipitated from strongly acid solutions, was somewhat soluble in water. It was readily soluble in ammonia and in alkaline sulphide solution. The sulphide yielded on ignition a white residue, soluble in water and in ammonia.

To an aqueous solution of the sulphide a little hydrofluoric acid was added and the solution saturated with solid potassium chloride. A heavy greyish-white gelatinous precipitate resulted.

These reactions agree throughout with the properties ascribed to germanium by Winkler. The boiling-point of the tetrachloride of germanium is 86°. The sulphide of germanium is white. It is soluble in water and in alkali and is precipitated only from strongly acid solutions. The formation of a double potassium fluoride is particularly characteristic.

From two portions of a solution of germanium sulphide in water the sulphide was precipitated with strong acid and hydrogen sulphide. The sulphide was filtered on a Gooch, dried at 110°, and weighed. It was then dissolved in ammonia and the crucibles re-weighed. The ammoniacal solutions were evaporated to dryness in platinum and the residues transformed to oxides by the method recommended by Winkler. The results follow:—

Determination	No. 1.	No. 2.
Weight of sulphide	0·0820	0·0812
Weight of oxide	0·0614	0·0604
Ratio oxide/sulphide	0·749	0·744

The theoretical ratio GeO_2/GeS_2 is 0·766, assuming the value 72·5 for the atomic weight of germanium.

A roughly quantitative determination of the amount of germanium present in the material was carried out as follows:—After distillation with hydrochloric acid and chlorine the sulphide was precipitated from the distillate with hydrogen sulphide. In some experiments the sulphide was weighed directly; in others it was transformed into oxide with nitric acid and weighed as GeO_2. The mean of several closely agreeing determinations gave the value $GeO_2 = 0{\cdot}25$ per cent.

To show whether or not germanium could be found in other zinc ores, samples of similar by-products from different ores were distilled with hydrochloric acid and chlorine. The distillates after dilution were treated with hydrogen sulphide. If no precipitate was obtained the test was considered negative. If a precipitate was obtained (other than the turbidity of sulphur) it was filtered off and transformed to oxide with nitric acid. The final test consisted in the formation from the residue of the double potassium fluoride with hydrofluoric acid and potassium chloride.

From several of the materials very definite confirmatory tests were obtained, others gave satisfactory blanks, while in only a few instances were the results uncertain. In none of the cases where positive results were secured was there found an amount of germanium at all comparable to that found in the material first examined, probably not one-tenth as much. A positive test was secured from Joplin ore and also from some Mexican ores. The Franklin ores gave negative results.

The germanium oxide prepared as described above has been examined spectroscopically by Dr. Burns, of the

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[*] Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Sir J. J. Dobbie, and Dr. M. O. Forster. (Drawn up by the Secretary). Read before the British Association (Section B), Newcastle Meeting, 1916.

Bureau of Standards, who reports as follows:—"It shows: Zinc, *absent*; lead, *weak*; silicon, *present*; tin, *fairly strong*; copper, *present* (possibly the last three were introduced accidentally by us); cadmium, *trace*; germanium, *principal constituent*; gallium, *present*; indium, *trace*."—*Journal of Industrial and Engineering Chemistry*, viii., No. 7.

REDUCTION OF COPPER OXIDE IN ALCOHOL VAPOUR IN REDUCING SUGAR DETERMINATIONS AND COPPER ANALYSIS.

By A. WEDDERBURN.

In the usual gravimetric invert sugar determination the reduced copper is weighed as Cu_2O, or after ignition as CuO. In weighing either oxide there is always some doubt as to the accuracy of the result. It is difficult to dry the cuprous oxide with certainty that some oxidation does not occur, and, further, the oxide is liable to be contaminated with organic matter, giving a high result. If ignited to the higher oxide great care is necessary that the oxidation be complete and that the crucible be not held in the reducing flame, the action of which would cause a partial reduction. Even if the cuprous oxide is heated in a muffle furnace considerable time and care are necessary to ensure a complete oxidation to CuO. The hygroscopic nature of cupric oxide makes it difficult to weigh with accuracy. In the hands of the ordinary laboratory assistant I have found a difference of as high as 12 mgrms. alter careful reignition of the weighed cupric oxide.

The ideal method is to weigh the copper in the metallic state. In accurate work the metal is obtained by the electrolytic method or by reducing the oxide in hydrogen. Both of these methods require considerable manipulation and time, also special apparatus not available in most sugar house laboratories.

With the purpose of simplifying the electrolytic method and avoiding the use of expensive platinum cathodes, I made some experiments in electrolytically depositing the copper directly from alundum crucibles on copper cathodes, with partial success. I found some difficulty in cleaning the copper cathodes perfectly prior to weighing. Mr. G. L. Spencer, chief chemist of the Cuban-American Sugar Company, advised that the copper could be readily cleaned by heating to redness and immersing in strong alcohol. This suggestion led to the reduction method described below.

The cleaning action of the alcohol is merely the reduction of the film of oxide to metallic copper, and it interested me to know to what extent a precipitate of copper oxide could be reduced by the same means. A precipitate of cuprous oxide was collected on an alundum crucible, washed with hot water, the crucible heated to redness and immersed in 95 per cent alcohol. The reduction was complete, the deposit of metallic copper adhering very firmly to the walls of the crucible. A number of trials with solutions of known strength gave very accurate results, but the shock to the crucibles was too great, many of them cracking after being used two or three times.

To avoid the breakage of crucibles the reduction was next tried in the vapour of alcohol and with entire success. The details of the method follow:—

Collect the suboxide of copper on an alundum filtering crucible, using Spencer's filtering funnels with suction. Thoroughly wash with hot water, followed by alcohol. Heat the crucible to redness a sufficient time to burn off any organic matter that may accompany the copper oxide. Allow the crucible to cool until the redness just begins to disappear, and then immerse it in an atmosphere of alcohol vapour as follows:—

Bend the wire ends of a small pipe stem or silica covered triangle so as to form a tripod support for the crucible and set the tripod on the bottom of a 400 cc. beaker, preferably of metal. Put into the beaker sufficient strong alcohol (denatured alcohol will answer) to cover the bottom to the depth of about 1 cm. and cover the beaker with a watch-glass. Heat the alcohol to boiling and continue heating until the vapours begin to condense on the under side of the cover glass, then place the hot crucible on the support above the alcohol and replace the cover glass. If the crucible is too hot the alcohol may take fire, but the flame may be readily extinguished by blowing directly on top of the cover glass, and no harm is done. Allow the alcohol to continue to boil a moment after putting in the crucible, then remove the beaker from the source of heat. The heat radiated from the crucible will prevent any further condensation of alcohol on the cover glass. The crucible should remain in the covered beaker until cooled to a temperature a little above that of the alcohol vapour, to prevent oxidation of the copper; about three or four minutes is sufficient. It may then be taken from the beaker and the cooling be finished in a desiccator, preliminary to weighing. If the crucible is quite cold when taken from the beaker it should be moistened with a little pure alcohol and this be burned, holding the crucible in an upright position. After the alcohol burns off the crucible is ready for cooling in the desiccator. A porcelain Gooch may be used if preferred.

The reduction to metallic copper is almost instantaneous and is complete. The results are identical with those by reduction in hydrogen, closely approximating the electrolytic method.

This method may be used in copper analysis, the separations being made in the usual way and the copper collected in any form readily burned to the oxide. If in form of copper sulphide the precipitate forms in clots and is burned to the oxide with difficulty. It is preferable to dry the sulphide, roast it gently, and then with a glass rod flattened at one end crush it to a powder. The rod should be wiped off with a piece of ashless filter-paper and the paper burned in the crucible. The heating may then be continued to drive off all sulphur and the oxide reduced in alcohol vapour.—*Journal of Industrial and Engineering Chemistry*, vii., No. 7.

THE DETECTION OF NATURAL AND ARTIFICIAL PIGMENTS IN OLEOMARGARINE AND BUTTER.*

By LEROY S. PALMER AND WALTER E. THRUN.

Introduction.

The natural yellow colour of butter and of the body-fat of dairy cattle, the latter being characterised by its intense colour in the case of the Guernsey and Jersey breeds, is now known to arise from the direct transfer of the yellow pigment, carotin, from the feed to the milk and body-fat. (Leroy S. Palmer and C. H. Eckles, "Carotin: the Natural Yellow Pigment of Milk Fat, &c.—*J. Biol. Chem.*, 1914, xvi., 191; Missouri Agr. Research, *Bulletins* 10 and 11, 1914). During the season of the year when the food of the dairy cow is more or less devoid of carotin and the butter in consequence loses its natural yellow colour the law permits the butter manufacturer to add certain harmless pigments to the butter in order that the consumers' demand for yellow butter throughout the year may be satisfied. Most of the various brands of "butter colour" on the market for this purpose are solutions of annatto in some vegetable oil, usually cottonseed oil. Certain other pigments are also permitted for butter colouring, but they are not in common use at the present time. (Among the permissible vegetable pigments are turmeric, saffron, marigold, and safflower. The only yellow or orange coal-tar dyes allowed under the Federal Law are Naphthol Yellow S and Orange I.

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* From *Journal of Industrial and Engineering Chemistry*, viii., No. 7.

The Federal Law also permits the use of the above-mentioned pigments for colouring oleomargarine, but at the same time imposes an additional tax of 10 cents per lb. on the coloured product. Oleomargarine mixed with highly coloured butter to give it a yellow colour, or manufactured from beef fat with a high natural yellow colour for the same purpose, is also subject to the colour tax. Many States have statutes with clauses to this effect. For example, the Missouri statutes declare that "to add to or mix with oleomargarine any artificial coloration that causes it to look like butter of any shade of yellow" renders the person so doing an oleomargarine manufacturer in the eyes of the law.

Although the Federal Law permits the use of colouring matter in the manufacture of oleomargarine, more than half the States of the Union have statutes which prohibit the sale of oleomargarine with any colour whatever, either natural or added. It is not possible for the manufacturers of oleomargarine to comply with the letter of this law because practically all beef fat contains some natural yellow colour, although it may not be possible to see this colour until the fat is rendered and viewed in the clear, liquid condition. The pigment of the natural beef fat is carotin, as previously stated. Its presence in the natural state in all beef fats makes it necessary for the Court to decide how much natural yellow colour is permissible under the law. The points for the chemist to determine in the case of suspected samples of oleomargarine are:—(1) Whether the oleomargarine has admixed with it sufficient butter to give it the colour found, and (2) whether the colour is natural to the fat or has been added. The material presented in this paper was the result of an effort to arrive at a satisfactory answer to the second of these questions in the case of several suspected samples of oleomargarine.

Experimental.

Satisfactory tests for most of the permissible dyes and vegetable pigments, including annatto, are given in all the text-books dealing with food analysis, and also in the official methods of the Association of Official Agricultural Chemists. Although a negative test for the usual artificial pigments employed in butter colouring would probably permit the conclusion that the colouring matter present was natural to the butter or oleomargarine, no simple, direct test for the natural pigment of animal fats is given.

Leach ("Food Inspection and Analysis," 3rd ed., 1914, 536, by Andrew L. Winton—John Wiley and Sons, New York), however, gives two tests for the detection of the colouring matter of the carrot when added to butter or oleomargarine—*i.e.*, Cornelison's ("A Method for Detecting Synthetic Colour in Butter"—*Journ. Am. Chem. Soc.*, 1908, xxx., 1478) and Moore's ("A Test for Carrot Colour in Butter"—*Analyst*, 1886, xi., 163) tests. Inasmuch as the carotin of butter and beef fat is now known to be chemically and physiologically identical with the carotin of carrots, one of two conclusions seemed obvious, either (1) the natural carotin of butter and beef fat exists in a different state than carotin added artificially to these fats, or (2) the tests are not specific for added carotin, as they are supposed to be.

Cornelison's Test.

Cornelison's test consists of shaking 10 grms. of fat with 10 to 20 grms. of 99·5 per cent acetic acid and adding a few drops of concentrated nitric and sulphuric acids respectively to 5 cc. portions of the clear acid extract. According to Leach this test applied to natural yellow butter gives a colourless extract, which remains colourless on adding nitric or sulphuric acids, while the acid extract from butter coloured with carrot colour is yellow, and remains yellow on addition of the nitric acid, but with sulphuric acid gives a pink colour on standing.

Reference to Cornelison's original article shows that the statement in Leach does not agree with the results stated by Cornelison in one very essential point—namely, that although Cornelison found the acid extract of natural butter to be colourless and to be unaffected by nitric acid, when treated with sulphuric acid the same faint pink coloration resulted as in the case of the extract of butter coloured with carotin from carrots. Leach's statement of Cornelison's tests is further contradicted and Cornelison's results substantiated by the following experiment:—

Ten cc. portions of natural yellow butter fat and colourless oleomargarine fat, coloured with carotin from carrots, were shaken in separatory funnels with 10 to 20 grms. of 99·5 per cent acetic acid. (This was done by contact of the rendered, melted oleomargarine with dried carrot pulp for several hours, with frequent shaking. The fat was filtered before using). The acid layer was drawn off when it became perfectly clear on standing. It had a faint yellow colour in each case, that from the oleomargarine possibly being a little more intense than that from the butter, due undoubtedly to the somewhat greater original colour of the oleomargarine. The addition of three drops of concentrated nitric acid to 5 cc. of each extract completely destroyed the yellow colour. The addition of three drops of concentrated sulphuric acid to 5 cc. of each extract produced a faint pink colour, which on standing for a few minutes persisted for some time.

Moore's Test.

Attention was next directed to Moore's test. The conclusion that would be drawn from the statement in Leach in regard to this test is that it was devised as a modification of Martin's general test, making it applicable as well for the detection of carotin (Edward W. Martin, "Detection of Artificial Colouring Matter in Butter Oleomargarine, Fats, Oils, &c."—*Analyst*, 1887, xii., 70). Five grms. of fat are shaken with 25 cc. of a reagent made by mixing 15 parts alcohol and 2 parts carbon disulphide. The alcohol layer which separates on standing contains any artificial colouring matter present in the fat). Leach states that "carotin (the colouring matter of the carrot root) does not impart its colour to the alcohol layer in Martin's test." "Moore has pointed out this exception, and shown that with carotin present the alcohol layer in Martin's test remains colourless, as in the case of uncoloured butter." Reference to the original papers by Martin and Moore makes it difficult to understand how this conception of the relation between the two tests could have arisen. Martin's test, which is given by Leach, was in reality published a year later than Moore's test, and was moreover a modification, making Moore's test applicable to the detection of a number of colouring matters, such as annatto, turmeric, aniline yellow, naphthol yellow, &c., and also included carotin. Martin states this specifically, and in addition states that "the natural colour of fats, oils, butter, &c., in no instance coloured the alcohol." However, reference to Moore's original paper shows that his test was in a certain sense a modification of an earlier test by Martin ("Detection of Annatto in Butter, &c."—*Analyst*, 1885, x., 163) for detecting annatto in oils and fats, in which the annatto is extracted from the fat with dillute caustic alkali. (This method is still in common use for extracting annatto from fats).

Martin's general test for artificial colouring matter has undoubtedly proved a useful one for the preliminary detection of the presence of artificial pigments. (The use of ether, acetone, &c., in the place of ethyl or methyl alcohol in the reagent, as suggested by Martin in his original paper, would not be possible if a separation of the fat from the solvent is desired, because the reagent made with ether, acetone, or other fat solvents would dissolve the fat or oil completely). Martin's test is not applicable, however, to the detection of either natural or added carotin in fat. Leach is correct in his statement in regard to this, but not in his statement that the exception for added carotin was pointed out by Moore.

Moore's test for added carotin in butter fat and other fats, as given in the original article, is to dissolve 10 grms. of fat in barely sufficient carbon disulphide, and to add to this 20 cc. of 90 per cent alcohol. A drop of dilute ferric chloride solution is now added and the tube containing the whole shaken. According to Moore, in the case of lard coloured artificially with carotin from carrots (prepared according to Husemann's method; August Husemann, "Ueber Carotin und Hydrocarotin," Liebig's *Ann.*, 1861, cxvii., 200), the addition of the ferric chloride caused the alcohol layer to "absorb the colour from the carbon disulphide layer until the tints of the two layers were reversed," while "natural butter without artificial colouring matter will not be decolorised by this treatment even after standing for several days." Moore states that he obtained the same results with beef fat, mutton fat, olive oil, and lard, coloured by warming them for several hours in contact with ground carrots, as he did in the case of the lard tested as noted above. No mention is made, however, of trying the test on butter fat coloured by carotin in this manner, the assumption being that the action would be similar.

To anyone familiar with the properties of carotin, particularly its relative solubility in different solvents, the principle which is supposed to be the basis of Moore's test is at once seen to be open to question. One of the well-established properties of carotin is its much greater solubility in carbon disulphide than in alcohol. That the mere addition of a drop of dilute ferric chloride solution should cause a reversion of this property would be questionable even if the carotin were merely dissolved in carbon disulphide; that this should occur when the matter is further complicated by the incorporation of the carotin in fat would be even more questionable.

Several preliminary trials of Moore's test were made on butter fat with a natural yellow colour. The results differed from Martin's in two respects: (1) the test was found to be specific for the carotin of natural yellow butter; (2) the phenomenon involved in the test was found to be merely a complete decolorisation of the pigment in the fat and not a transfer of the carotin from the fat to the alcohol layer. Although the alcohol layer had a yellowish tint at the conclusion of the tests no carotin was found to be present. An attempt to recover carotin as unsaponifiable matter after saponification of the fat which was in solution in the alcohol gave negative results. The yellow colour of the alcohol layer, which led Moore to believe that carotin had been extracted by the alcohol and ferric chloride, is undoubtedly caused by the ferric chloride itself. Moore himself stated that the pigment in the alcohol layer in his test failed to give a green coloration with ferric chloride, which is one of the properties of carotin given by Husemann. (It seems probable that Moore's test grew out of his attempt to test for carotin with ferric chloride, according to its property, as stated by Husemann, of giving a green coloration with this reagent when in alcoholic solution. Instead he got a decolorisation of the fat. Moore does not state the origin of the test in his original paper).

(To be continued).

Causes of Error affecting Atomic Weight Determinations. Gaseous Impurities in Silver.—Ph. A. Guye and F. E. E. Germann.—The authors have shown that in certain conditions silver may retain traces of gas after hydrogen has been bubbled through the fused metal, and these traces may appreciably modify atomic weights referred to silver. The distribution of the gas in the metal may not be uniform, varying considerably from the outer to the central parts. Specimens of metal used for atomic weight determinations must be carefully investigated from the point of view of gaseous impurities, and modern methods must be used, not based upon the old method of heating *in vacuo*.—*Journal de Chimie Physique*, 1916, xiv., No. 2).

NOTICES OF BOOKS.

Vinegar: Its Manufacture and Examination. By C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C. London: Charles Griffin and Co., Ltd. 1916. Pp. xvi.+201. Price 8s. 6d. net.

No book devoted exclusively to the chemistry and manufacture of vinegar has hitherto been published in the English language, partly owing to the fact that the secrets of its preparation have been jealously guarded by those engaged in it. This book, which gives a very interesting account of the different branches of the subject, will be cordially welcomed by chemists and manufacturers. It contains a clear exposition of the scientific principles of the manufacture, giving, first, an account of early theories of acetification and of the work of Pasteur and others. The chemistry and biology of the acetic bacteria is well treated, the pages on the subject being very fully illustrated. Details of methods of manufacture, including the older, which are now of historical interest only, as well as modern methods are described, and a general account is given of the analysis of vinegar and the interpretation of the results is discussed. The book will certainly fill a gap not satisfactorily filled by articles in the chemical dictionaries and in text-books of applied chemistry, and the author is to be congratulated upon having very efficiently done a useful piece of work in its preparation.

Trade as a Science. By Ernest J. P. Benn. With an Introductory Preface by the Rt. Hon. Lord Burnham, M.A. London: Jarrold and Sons. Pp. 184. Price 2s. 6d. net.

This little book is written in a distinctly constructive spirit, and as such deserves very careful study. The schemes put forward in it are naturally open to criticism, but at any rate they are definite and detailed and calculated to set men thinking and perhaps planning afresh. It is indisputably quite time that we began to consider seriously the question of the future of British trade after the war, and it is equally true that public opinion needs a good deal of educating on the subject. This book is devoted to the discussion of the organisation of trade. The author first gives a *résumé* of the present state of affairs as observed in his experience as a commercial journalist. He points out the faults both of the system and of individuals, and gives warnings of the impending difficulties and of the danger of letting their settlement become a question of party politics. He then proceeds to explain his scheme for the Ministry of Commerce, going into details of personnel and salaries, and discussing at some length the duties of the different officials. He also makes suggestions relating to the constitution of a model trade association, and in later chapters deals shortly with the questions of industrial and scientific research and commercial education, the latter being a subject upon which he has practical suggestions to offer. In the chapter on labour he writes in a liberal and temperate spirit, with a clear idea of the difficulties and of the best way to approach them, and the book represents a sincere attempt to view our present position in a right light and suggest some means of improvement.

Le Chimie Raisonnée ("Rational Chemistry"). By M. Lemarchands. Grenoble: Jules Rey. Paris: Gauthier-Villars et Cie. 1914. Pp. 1713. Price 5 francs.

The author of this book endeavours to show his readers that chemistry is not a science the study of which calls into play the memory only or even chiefly, but is one in which the exercise of the reasoning power should play the most important part. He writes more especially for engineering students, for whom a knowledge of inorganic chemistry is indispensable, and who frequently regard the subject merely as an accumulation of a vast number of more or less unrelated facts. He discusses in the first part the general properties of substances dealing first with the elements and then with acids, bases, and salts. In Part II. general methods of preparation are described, and the theory of ions is developed in the third part. Finally some account is given of the most profitable way to apply the principles worked out in the first three parts to the study of individual substances. While it does not appear probable that anyone would find it possible to learn chemistry from the book, the use of it as a commentary upon and summary of more detailed works would lighten the student's labours. The concise general statements, tabular *résumés*, and very clear type are good features, and within the limits mentioned above it should certainly prove useful.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxii. No. 25, June 19, 1916.

The $T_{7\cdot8}$ and $T_{5\cdot6}$ Isomers of Stearolic Acid.—S. Posternak.—Of the sixteen normal chain acetylenic acids, $C_{18}H_{32}O_2$, which theoretically exist only four have been described—stearolic acid, $T_{9\cdot10}$; tariric acid, $T_{6\cdot7}$; and the $T_{10\cdot11}$ and $T_{8\cdot9}$ acids. The knowledge of the whole series of these isomers and of their many crystallised derivatives would be of great importance in the study of the relation between the chemical constitution and the physical properties of these substances, and the author has occupied himself with their preparation and the study of their properties. He obtained the isomers $T_{7\cdot8}$ and $T_{5\cdot6}$ by fusing tariric acid and passing in a current of dry hydriodic acid. The heavy brown oil thus obtained was dissolved in alcoholic potash and heated on the water-bath, the potassium iodide was filtered off, the alcohol distilled, and the soaps in solution were decomposed by dilute sulphuric acid. On cooling, crystals mixed with a certain amount of oily monoiodooleic acids were deposited. These crystals consisted of the three stearolic isomers, $T_{7\cdot8}$, $T_{6\cdot7}$, and $T_{5\cdot6}$. To separate them they were dissolved in alcohol and alcoholic soda was added. The acid salts thus obtained were decomposed by means of dilute sulphuric acid, and on crystallisation pure tariric acid separated. The $T_{7\cdot8}$ isomer was then removed in the form of its diiodo derivative. The $T_{5\cdot6}$ isomer was separated by adding fractions of alcoholic soda and crystallising the acid salts in fractions. The free acid was liberated in each fraction and recrystallised.

No. 26, June 26, 1916.

This number contains no chemical matter.

Vol. clxiii., No. 1, July 3, 1916.

Acid Hæmochromogen.—Ch. Dhéré and G. Vegezzi.—When a very slightly acid solution of pure hæmatin in alcohol is reduced by means of powdered sodium hydrosulphite in a sealed tube, acid hæmochromogen is obtained. Like ordinary alkaline hæmochromogen it has an absorption spectrum showing three bands which in clearness, intensity, and breadth closely resemble those of alkaline hæmochromogen. They differ from them, however, in position. The authors believe that acid hæmochromogen is actually the free compound.

No. 2, July 10, 1916.

Thermo-electric Measurement of the Critical Points of Iron.—George K. Burgess and H. Scott.—By a modification of the method of Boudouard and Le Chatelier both the A_2 and A_3 points were clearly shown in pure iron (99·968 per cent). A thread of iron was soldered at its two ends to the junctions of two Le Chatelier couples, and placed in the centre of an electric resistance furnace with automatic control. The deviation of a galvanometer connected to the two platinum threads of the couple was read, which was a measure of the thermo-electric force of the iron-platinum couple for a fall of temperature of less than 10°. The temperatures of the two extremities of the iron were given by the couples by the potentiometric method.

No. 3, July 17, 1916.

Biochemical Synthesis of a Galactobiose.—Em. Bourquelot and A. Aubry.—By the action of emulsin and a little toluene on an aqueous solution of galactose the authors have synthesised a galactobiose, although they have not succeeded in obtaining the product in a crystalline state. The properties of its osazone show that it is a hexabiose. Its rotatory power has been determined and has been found to be $\alpha_D' = +54{\cdot}1^{\circ}$ in water at 19°, $+39{\cdot}3^{\circ}$ in alcohol at 90°, and $+49{\cdot}18^{\circ}$ in alcohol at 40°. The galactobiose has been shown to be hydrolysable by emulsin, and thus the theory of reversibility has been verified.

No. 4, July 24, 1916.

Absorption of Ultra-violet Radiations by Bromine Derivatives of Methane.—MM. Massol and Faucon.—The authors have studied the absorption of ultra-violet radiations by bromine, carbon tetrabromide, tribromomethane, and dibromomethane. The characteristic band of bromine in solution, λ 295 to 248, was not found in any of the bromine derivatives of methane. The less bromine they contain the more transparent the compounds are towards the ultra-violet radiations. Each bromine derivative is less transparent than the corresponding chlorine derivative, examined in the same conditions as regards concentration and thickness.

Density of Gaseous Hydrobromic Acid. Contribution to the Revision of the Atomic Weight of Bromine.—E. Moles.—Hydrobromic acid gas was prepared by the action of bromine upon paraffin heated to 200°. The excess of bromine was fixed by passing the gas through a paraffin washer heated to 180°, and the gas was purified by fractional distillation. The mean value of the weight of the normal litre deduced from 33 determinations made with specimens prepared by four different methods is $3{\cdot}64442 \pm 0{\cdot}00013$ grm. This gives for the atomic weight of bromine ($H = 1{\cdot}008$) the value 79·926.

Bulletin de la Société Chimique de France. Vol. xix.-xx., No. 6, 1916.

Kinetics of the Saponification of Pyrrolic Derivatives.—G. Korschun.—The author has made a very thorough study of the velocities of saponification of pyrrolic derivatives, and has tabulated the results. He employed pyrrol-monocarbonic ethers at 50°, dicarbonic ethers at 50°, pyrrol-dicarbonic ether acids at 50°, and all three classes of compounds at 98·3—98·7° Some of the general conclusions to be drawn are as follows:—The replacement of the hydrogen attached to the nitrogen by the CH_3 group, or NH_2 or C_6H_5, increases by varying amounts the velocity of the saponification, while the replacement of a hydrogen in the 4-position decidedly reduces it. Other things being equal, the carboxethyl of a pyrrolic ether is much easier to saponify when it is in the α than in the β position. The carboxethyls of the mono and dicarbonic pyrrol ethers in the α position are saponified at about the same rates. One of the carboxethyls of the pyrrol-3·4-dicarbonic ethers is much easier to saponify than the corresponding carboxethyl of the pyrrol monocarbonic ethers, but the second group is saponified far more slowly than the first. The replacement of the two methyls of the 2·5 dimethyl-pyrrol-3-4-dicarbonic ether by two phenyls considerably diminishes the rate of saponification.

Graphitic Acid.—L. Balbiano.—The author has prepared graphitic acid from three varieties of graphite, two natural and one artificial, using different methods of oxidation. The graphitic acid from natural graphites, when the excess of permanganate is decomposed by means of hydrogen peroxide, is crystalline and yellow, but when it is washed and dried it turns brown and a yellowish brown powder is obtained on pulverisation. The graphitic acid obtained from Acheson graphite is ochre-coloured. By analysing the products by gradual heating the author found that the composition was not constant, the formula varying between $C_{13}H_4O_7$ and $C_{14}H_4O_7$. The green graphitic oxide has the same composition as the acid. In studying the action of various reagents on the graphitic products it was found that baryta merely absorbs the CO_2, being transformed slowly in the cold and rapidly on heating into barium carbonate.

MISCELLANEOUS.

Solubility of Caustic Soda in Liquid Ammonia.—Nicholas Tchitchinadze.—The author has constructed an apparatus by means of which determinations of solubility in liquid ammonia can be made, eliminating the influence of the impurities which come from the air. The same apparatus can be slightly modified for indirect measurements of solubility by finding the electrical conductivity of the saturated solution. It was found that the solubility of NaOH in liquid ammonia is about 1·8 mgrm. per litre, which confirms the observation of Franklin and Kraus. The presence of traces of humidity in liquid ammonia exercises a considerable influence upon the solubility of NaOH.

The Bonecourt Waste Heat Boiler Company, Ltd., of Parliament Mansions, Victoria Street, has recently issued a new catalogue, "The Book of Bonecourt Boilers," which engineers will find of considerable interest. The advantages of the improved Surface Combustion System are put forward, the boilers are described in detail, and statistics of efficiency, &c., are given, together with an interesting table of some well-known sources of waste heat.

Application of Scientific Method to Brewing Practice.—The *Journal of the Institute of Brewing* (vol. xxii., No. 5), contains a full reproduction of the very interesting Address delivered by Dr. Horace T. Brown on the occasion of the presentation of his portrait by the members of the Institute. Dr. Horace Brown took for his subject "Fifty Years' Experience of the Application of Scientific Method to Brewing Practice," and hardly anyone in the scientific world is better qualified to discuss the subject, for he has seen brewing emerge from the rule-of-thumb state to its present position among the industries, and has himself played an important *rôle* in its development. Perhaps the most interesting part of the Address was the account of Pasteur's work and the comparison of it with that of Lister, while the pages on Pure Yeast Culture and Yeast Purification contain many important suggestions for future research work.

British Association of Trade and Technical Journals.—The First Annual Meeting of members will be held at the Hotel Cecil, on Monday, October 2, 1916, at 12 o'clock noon, to receive the Council's Report and Accounts, to elect officers snd members of the Council, and to appoint auditors. The whole of the council retire from office, but are eligible for re-election. Nominations of new candidates for election should be sent to the Secretary not later than five days before the meeting, in order that their names may be included in the ballot paper.—T. C. Alder, Hon. Secretary.

Mansion House Engineering Meeting.—In view of the national prominence of the engineering industry, the Lord Mayor is convening a public meeting at the Mansion House, at 3 p.m., on Wednesday, September 20, to discuss future trade policy with special reference to the economic utilisation of the engineering works of the nation which have been so largely expanded in capacity and equipment during the past two years. The organisation of the meeting is being undertaken by the British Electrical and Allied Manufacturers' Association, with the support of the British Engineers' Association, the British Empire Producers' Organisation, and the Engineering and Electrical Sections of the London Chamber of Commerce. Applications for tickets of admission should be sent to Mr. T. C. Elder, Organising Secretary for the Meeting, B.E.A.M.A., Offices, 36, Kingsway, London, W.C., or to the secretaries of any of the above organisations.

Exhibition of British-made Glass and Laboratory Ware.—This Exhibition at the Institute of Chemistry will remain open to chemists until the end of September. The Firms exhibiting apparatus are as follows:—

Laboratory Glassware.—Messrs. Baird and Tatlock (London), Ltd., 14, Cross Street, Hatton Garden, London, E.C. The British Laboratory Ware Association, Ltd., 31—34, Basinghall Street, London, E.C. The Edinburgh and Leith Flint Glass Co., Norton Park, Edinburgh. Messrs. John Moncrieff, Ltd., Perth. Messrs. Wood Bros. Glass Co., Ltd., Borough Flint Glass Works, Barnsley, Yorks. (London Agent: Messrs. W. Toogood, Ltd., 77, Southwark Street, S.E.).

Miners' Lamp Glasses.—Messrs. Ackroyd and Best, Ltd., Morley, near Leeds.

Laboratory Porcelain.—Messrs. Doulton and Co., Ltd., Royal Doulton Potteries, Lambeth, London, S.E. The Worcester Royal Porcelain Co., Ltd., Worcester.

Thermometer Tubing.—Messrs. James Powell and Son, Whitefriars Glass Works, Tudor Street, London, E.C. Messrs. Frank Tomey and Co., Ltd., Borough Glass Works, 263, Victoria Road, Aston, Birmingham.

Filter-paper.—Messrs. W. and R. Balston, Ltd., Springfield Mills, Maidstone, Kent. (London Agent: Messrs. H. Reeve Angel and Co., 15, New Bridge Street, London, E.C.

Institute of Metals.—The following is a list of the Papers to be submitted at the Autumn Meeting to be held at the Rooms of the Chemical Society, on Wednesday, September 20, 1916.—

"The Allotropy of Silver." By Dr. W. D. Helderman (Utrecht University, Holland).

"Cadmium in Spelter." By W. R. Ingalls (New York).

"The Annealing of Arsenical Brass containing 61 and 62·5 per cent of Copper. A Study of the Structure and Properties Developed by Varying the Rate of Cooling within the Transformation Range." By C. H. Mathewson and E. M. Thalheimer (Yale University, U.S.A.).

"The Development of the Spelter Industry." By Ernest A. Smith, A.R.S.M. (Sheffield).

It is hoped to be able to supply Members intending to take part in the Discussion of any Paper with a copy of such Paper on application being made to the Secretary a few days before the Meeting, but on the present occasion, owing to printer's difficulties, this cannot be guaranteed. Copies of all the Papers will, however, almost certainly be available at the Meeting for the use of Members, and those who are unable to attend will subsequently be supplied, on application, with a copy of any Paper of which prints remain. In the Discussion following the reading of the Papers each speaker will be limited to ten minutes unless the time should be extended by the Chairman. Speakers who are unable to give more than a summary of their views in the time available may send a written statement to the Secretary for publication in the December issue of the *Journal*, such statement to be in the hands of Secretary not later than noon on Friday, October 20, 1916.—G. Shaw Scott, Secretary.

THE CHEMICAL NEWS.

Vol. CXIV., No. 2965.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SCIENCE SECTION OF THE BRITISH ASSOCIATION.

Newcastle-on-Tyne, 1916.

By Prof. A. N. WHITEHEAD, Sc.D., F.R.S.,
President of the Section.

The Organisation of Thought.

The subject of this address is the organisation of thought, a topic evidently capable of many diverse modes of treatment. I intend more particularly to give some account of that department of logical science with which some of my own studies have been connected. But I am anxious, if I can succeed in so doing, to handle this account so as to exhibit the relation with certain considerations which underlie general scientific activities.

It is no accident that an age of science has developed into an age of organisation. Organised thought is the basis of organised action. Organisation is the adjustment of diverse elements so that their mutual relations may exhibit some predetermined quality. An epic poem is a triumph of organisation; that is to say, it is a triumph in the unlikely event of it being a good epic poem. It is the successful organisation of multitudinous sounds of words, associations of words, pictorial memories of diverse events and feelings ordinarily occurring in life, combined with a special narrative of great events: the whole so disposed as to excite emotions which, as defined by Milton, are simple, sensuous, and passionate. The number of successful epic poems is commensurate, or, rather, is inversely commensurate with the obvious difficulty of the task of organisation.

Science is the organisation of thought. But the example of the epic poem warns us that science is not any organisation of thought. It is an organisation of a certain definite type which we will endeavour to determine.

Science is a river with two sources, the practical source and the theoretical source. The practical source is the desire to direct our actions to achieve predetermined ends. For example, the British nation, fighting for justice, turns to science, which teaches it the importance of compounds of nitrogen. The theoretical source is the desire to understand. Now I am going to emphasise the importance of theory in science. But to avoid misconception I most emphatically state that I do not consider one source as in any sense nobler than the other, or intrinsically more interesting. I cannot see why it is nobler to strive to understand than to busy oneself with the right ordering of one's actions. Both have their bad sides; there are evil ends directing actions, and there are ignoble curiosities of the understanding.

The importance, even in practice, of the theoretical side of science arises from the fact that action must be immediate, and takes place under circumstances which are excessively complicated. If we wait for the necessities of action before we commence to arrange our ideas, in peace we shall have lost our trade, and in war we shall have lost the battle.

Success in practice depends on theorists who, led by other motives of exploration, have been there before, and by some good chance have hit upon the relevant ideas. By a theorist I do not mean a man who is up in the clouds, but a man whose motive for thought is the desire to formulate correctly the rules according to which events occur. A successful theorist should be excessively interested in immediate events, otherwise he is not at all likely to formulate correctly anything about them. Of course both sources of science exist in all men.

Now, what is this thought organisation which we call science? The first aspect of modern science which struck thoughtful observers was its inductive character. The nature of induction, its importance, and the rules of inductive logic have been considered by a long series of thinkers, especially English thinkers—Bacon, Herschel, J. S. Mill, Venn, Jevons, and others. I am not going to plunge into an analysis of the process of induction. Induction is the machinery and not the product, and it is the product which I want to consider. When we understand the product we shall be in a stronger position to improve the machinery.

First, there is one point which it is necessary to emphasise. There is a tendency in analysing scientific processes to assume a given assemblage of concepts applying to nature, and to imagine that the discovery of laws of nature consists in selecting by means of inductive logic some one out of a definite set of possible alternative relations which may hold between the things in nature answering to these obvious concepts. In a sense this assumption is fairly correct, especially in regard to the earlier stages of science. Mankind found itself in possession of certain concepts respecting nature—for example, the concept of fairly permanent material bodies—and proceeded to determine laws which related the corresponding percepts in nature. But the formulation of laws changed the concepts, sometimes gently by an added precision, sometimes violently. At first this process was not much noticed, or at least was felt to be a process curbed within narrow bounds, not touching fundamental ideas. At the stage where we now are, the formulation of the concepts can be seen to be as important as the formulation of the empirical laws connecting the events in the universe as thus conceived by us. For example, the concepts of life, of heredity, of a material body, of a molecule, of an atom, of an electron, of energy, of space, of time, of quantity, and of number. I am not dogmatising about the best way of getting such ideas straight. Certainly it will only be done by those who have devoted themselves to a special study of the facts in question. Success is never absolute, and progress in the right direction is the result of a slow, gradual process of continual comparison of ideas with facts. The criterion of success is that we should be able to formulate empirical laws, that is, statements of relations, connecting the various parts of the universe as thus conceived, laws with the property that we can interpret the actual events of our lives as being our fragmentary knowledge of this conceived interrelated whole.

But, for the purposes of science, what is the actual world? Has science to wait for the termination of the metaphysical debate till it can determine it own subject-matter? I suggest that science has a much more homely starting-ground. Its task is the discovery of the relations which exist within that flux of perceptions, sensations, and emotions which forms our experience of life. The panorama yielded by sight, sound, taste, smell, touch, and by more inchoate sensible feelings, is the sole field of its activity. It is in this way that science is the thought organisation of experience. The most obvious aspect of this field of actual experience is its disorderly character. It is for each person a *continuum*, fragmentary, and with elements not clearly differentiated. The comparison of the sensible experiences of diverse people brings its own difficulties. I insist on the radically untidy, ill-adjusted character of the fields of actual experience from which science starts. To grasp this fundamental truth is the first step in wisdom when constructing a philosophy of science. This fact is concealed by the influence of language, moulded by science, which foists on us exact concepts as though they represented the immediate deliverances of experience. The result is that we imagine that we have immediate experience of a world of perfectly defined objects implicated in perfectly defined events which, as known to us by the direct deliverance of our senses, happen at exact instants of time, in a space formed by exact points, without parts and without magnitude: the neat, trim, tidy, exact world which is the goal of scientific thought.

My contention is that this world is a world of ideas, and that its internal relations are relations between abstract concepts, and that the elucidation of the precise connection between this world and the feelings of actual experience is the fundamental question of scientific philosophy. The question which I am inviting you to consider is this: How does exact thought apply to the fragmentary, vague *continua* of experience? I am not saying that it does not apply, quite the contrary. But I want to know how it applies. The solution I am asking for is not a phrase however brilliant, but a solid branch of science, constructed with slow patience, showing in detail how the correspondence is effected.

The first great steps in the organisation of thought were due exclusively to the practical source of scientific activity, without any admixture of theoretical impulse. Their slow accomplishment was the cause and also the effect of the gradual evolution of moderately rational beings. I mean the formation of the concepts of definite material objects, of the determinate lapse of time, of simultaneity, of recurrence, of definite relative position, and of analogous fundamental ideas, according to which the flux of our experience is mentally arranged for handy reference; in fact, the whole apparatus of common-sense thought. Consider in your mind some definite chair. The concept of that chair is simply the concept of all the interrelated experiences connected with that chair – namely, of the experiences of the folk who made it, of the folk who sold it, of the folk who have seen it or used it, of the man who is now experiencing a comfortable sense of support, combined with our expectations of an analogous future, terminated finally by a different set of experiences when the chair collapses and becomes fire-wood. The formation of that type of concept was a tremendous job, and zoologists and geologists tell us that it took many tens of millions of years. I can well believe it.

I now emphasise two points. In the first place, science is rooted in what I have just called the whole apparatus of common-sense thought. That is the *datum* from which it starts, and to which it must recur. We may speculate, if it amuses us, of other beings in other planets who have arranged analogous experiences according to an entirely different conceptual code—namely, who have directed their chief attention to different relations between their various experiences. But the task is too complex, too gigantic, to be revised in its main outlines. You may polish up common sense, you may contradict it in detail, you may surprise it. But ultimately your whole task is to satisfy it.

In the second place, neither common sense nor science can proceed with their task of thought organisation without departing in some respect from the strict consideration of what is actual in experience. Think again of the chair. Among the experiences upon which its concept is based I included our expectations of its future history. I should have gone further and included our imagination of all the possible experiences which in ordinary language we should call perceptions of the chair which might have occurred. This is a difficult question, and I do not see my way through it. But at present in the construction of a theory of space and of time there seem insuperable difficulties if we refuse to admit ideal experiences.

This imaginative perception of experiences, which, if they occurred, would be coherent with our actual experiences, seems fundamental in our lives. It is neither wholly arbitrary nor yet fully determined. It is a vague background which is only made in part definite by isolated activities of thought. Consider, for example, our thoughts of the unseen flora of Brazil.

Ideal experiences are closely connected with our imaginative reproduction of the actual experiences of other people, and also with our almost inevitable conception of ourselves as receiving our impressions from an external complex reality beyond ourselves. It may be that an adequate analysis of every source and every type of experience yields demonstrative proof of such a reality and of its nature. Indeed, it is hardly to be doubted that this is the case. The precise elucidation of this question is the problem of metaphysics. One of the points which I am urging in this address is that the basis of science does not depend on the assumption of any of the conclusions of metaphysics; but that both science and metaphysics start from the same given groundwork of immediate experience, and in the main proceed in opposite directions on their diverse tasks.

For example, metaphysics inquires how our perceptions of the chair relate us to some true reality. Science gathers up these perceptions into a determinate class, adds to them ideal perceptions of analogous sort, which under assignable circumstances would be obtained, and this single concept of that set of perceptions is all that science needs; unless indeed you prefer that thought find its origin in some legend of those great twin brethren, the Cock and Bull.

My immediate problem is to inquire into the nature of the texture of science. Science is essentially logical. The nexus between its concepts is a logical nexus, and the grounds for its detailed assertions are logical grounds. King James said, "No bishops, no King." With greater confidence we can say, "No logic, no science." The reason for the instinctive dislike which most men of science feel towards the recognition of this truth is, I think, the barren failure of logical theory during the past three or four centuries. We may trace this failure back to the worship of authority which in some respects increased in the learned world at the time of the Renaissance. Mankind then changed its authority, and this fact temporarily acted as an emancipation. But the main fact, and we can find complaints (*e.g.*, in 1551 by Italian schoolmen) of it at the very commencement of the modern movement, was the establishment of a reverential attitude towards any statement made by a classical author. Scholars became commentators on truths too fragile to bear translation. A science which hesitates to forget its founders is lost. To this hesitation I ascribe the barrenness of logic. Another reason for distrust of logical theory and of mathematics is the belief that deductive reasoning can give you nothing new. Your conclusions are contained in your premises, which by hypothesis are known to you.

In the first place this last condemnation of logic neglects the fragmentary, disconnected character of human knowledge. To know one premise on Monday, and another premise on Tuesday, is useless to you on Wednesday. Science is a permanent record of premises, deductions, and conclusions, verified all along the line by its correspondence with facts. Secondly, it is untrue that when we know the premises we also know the conclusions. In arithmetic, for example, mankind are not calculating boys. Any theory which proves that they are conversant with the consequences of their assumptions must be wrong. We can imagine beings who possess such insight. But we are not such creatures. Both these answers are, I think, true and relevant. But they are not satisfactory. They are too much in the nature of bludgeons, too external. We want something more explanatory of the very real difficulty which the question suggests. In fact, the true answer is embedded in the discussion of our main problem of the relation of logic to natural science.

It will be necessary to sketch in broad outline some relevant features of modern logic. In doing so I shall try to avoid the profound general discussions and the minute technical classifications which occupy the main part of traditional logic. It is characteristic of a science in its earlier stages—and logic has become fossilised in such a stage—to be both ambitiously profound in its aims and trivial in its handling of details. We can discern four departments of logical theory. By an analogy which is not so very remote I will call these departments or sections the arithmetic section, the algebraic section, the section of general-function theory, the analytic section. I do not mean that arithmetic arises in the first section, algebra in the second section, and so on; but the names are suggestive of certain qualities of thought in each section which are reminiscent of analogous qualities in arithmetic, in algebra, in the general theory of a mathematical function, and in the analysis of the properties of particular functions.

The first section—namely, the arithmetic stage—deals with the relations of definite propositions to each other, just as arithmetic deals with definite numbers. Consider any definite proposition; call it "p." We conceive that there is always another proposition which is the direct contradictory to "p"; call it "not-p." When we have got two propositions, p and q, we can form derivative propositions from them and from their contradictories. We can say, "At least one of p or q is true, and perhaps both." Let us call this proposition "p or q." I may mention as an aside that one of the greatest living philosophers has stated that this use of the word "or"—namely, "p or q" in the sense that either or both may be true—makes him despair of exact expression. We must brave his wrath, which is unintelligible to me.

We have thus got hold of four new propositions, namely, "p or q," and "not-p or q," and "p or not-q," and "not-p or not-q." Call these the set of disjunctive derivatives. There are, so far, in all eight propositions, p, not-p, q, not-q, and the four disjunctive derivatives. Any pair of these eight propositions can be taken and substituted for p and q in the foregoing treatment. Thus each pair yields eight propositions, some of which may have been obtained before. By proceeding in this way we arrive at an unending set of propositions of growing complexity, ultimately derived from the two original propositions p or q. Of course only a few are important. Similarly we can start from three propositions, p, q, r, or from four propositions, p, q, r, s, and so on. Any one of the propositions of these aggregates may be true or false. It has no other alternative. Whichever it is, true or false, call it the "truth-value" of the proposition.

The first section of logical enquiry is to settle what we know of the truth-values of these propositions, when we know the truth-values of some of them. The enquiry, so far as it is worth while carrying it, is not very abstruse, and the best way of expressing its results is a detail which I will not now consider. This enquiry forms the arithmetic stage.

The next section of logic is the algebraic stage. Now, the difference between arithmetic and algebra is that in arithmetic definite numbers are considered, and in algebra symbols—namely, letters—are introduced which stand for any numbers. The idea of a number is also enlarged. These letters, standing for any numbers, are called sometimes variables and sometimes parameters. Their essential characteristic is that they are undetermined, unless, indeed, the algebraic conditions which they satisfy implicitly determine them. Then they are sometimes called unknowns. An algebraic formula with letters is a blank form. It becomes a determinate arithmetic statement when definite numbers are substituted for the letters. The importance of algebra is a tribute to the study of form. Consider now the following proposition,

The specific heat of mercury is 0·033.

This is a definite proposition which, with certain limitations, is true. But the truth-value of the proposition does not immediately concern us. Instead of mercury put a mere letter which is the name of some undetermined thing; we get,

The specific heat of x is 0·033.

This is not a proposition; it has been called by Russell a propositional function. It is the logical analogy of an algebraic expression. Let us write $f(x)$ for any propositional function.

We could also generalise still further, and say,

The specific heat of x is y.

We thus get another propositional function, $F(x, y)$ of two arguments x and y, and so on for any number of arguments.

Now, consider $f(x)$. There is the range of values of x, for which $f(x)$ is a proposition, true or false. For values of x outside this range, $f(x)$ is not a proposition at all, and is neither true nor false. It may have vague suggestions for us, but it has no unit meaning of definite assertion. For example,

The specific heat of water is 0·033

is a proposition which is false; and

The specific heat of virtue is 0·033

is, I should imagine, not a proposition at all; so that it is neither true nor false, though its component parts raise various associations in our minds. This range of values, for which $f(x)$ has sense, is called the "type" of the argument x.

But there is also a range of values of x for which $f(x)$ is a true proposition. This is the class of those values of the argument which *satisfy* $f(x)$. This class may have no members, or, in the other extreme, the class may be the whole type of the arguments.

We thus conceive two general propositions respecting the indefinite number of propositions which share in the same logical form, that is, which are values of the same propositional function. One of these propositions is,

$f(x)$ yields a true proposition for each value of x of the proper type;

the other proposition is,

There is a value of x for which $f(x)$ is true.

Given two, or more, propositional functions $f(x)$ and $\phi(x)$ with the same argument x, we form derivative propositional functions, namely,

$f(x)$ or $\phi(x)$, $f(x)$ or not-$\phi(x)$,

and so on with the contradictories, obtaining, as in the arithmetical stage, an unending aggregate of propositional functions. Also each propositional function yields two general propositions. The theory of the interconnection between the truth-values of the general propositions arising from any such aggregate of propositional functions forms a simple and elegant chapter of mathematical logic.

In this algebraic section of logic the theory of types crops up, as we have already noted. It cannot be neglected without the introduction of error. Its theory has to be settled at least by some safe hypothesis, even if it does not go to the philosophic basis of the question. This part of the subject is obscure and difficult, and has not been finally elucidated, though Russell's brilliant work has opened out the subject.

The final impulse to modern logic comes from the independent discovery of the importance of the logical variable by Frege and Peano. Frege went further than Peano, but by an unfortunate symbolism rendered his work so obscure that no one fully recognised his meaning who had not found it out for himself. But the movement has a large history reaching back to Liebniz and even to Aristotle. Among English contributors are De Morgan, Boole, and Sir Alfred Kempe; their work is of the first rank.

The third logical section is the stage of general-function theory. In logical language, we perform in this stage the transition from intension to extension, and investigate the theory of denotation. Take the propositional function $f(x)$. There is the class, or range of values for x, whose members satisfy $f(x)$. But the same range may be the class whose members satisfy another propositional function $\phi(x)$. It is necessary to investigate how to indicate the class by a way which is indifferent as between the various propositional functions which are satisfied by any member of it, and of it only. What has to be done is to analyse the nature of propositions about a class—namely, those propositions whose truth-values depend on the class itself and not on the particular meaning by which the class is indicated.

Furthermore, there are propositions about alleged individuals indicated by descriptive phrases: for example, propositions about "the present King of England," who does exist, and "the present Emperor of Brazil," who does not exist. More complicated, but analogous, questions involving propositional functions of two variables involve the notion of "correlation," just as functions of one argument involve classes. Similarly functions of three arguments yield three-cornered correlations, and so on. This logical section is one which Russell has made peculiarly his own by work which must always remain fundamental. I have called this the section of functional theory, because its ideas are essential to the construction of logical denoting functions which include as a special case ordinary mathematical functions such as sine, logarithm, &c. In each of these three stages it will be necessary gradually to introduce an appropriate symbolism, if we are to pass on to the fourth stage.

The fourth logical section, the analytic stage, is concerned with the investigation of the properties of special logical constructions, that is, of classes and correlations of special sorts. The whole of mathematics is included here. So the section is a large one. In fact, it is mathematics, neither more nor less. But it includes an analysis of mathematical ideas not hitherto included in the scope of that science, nor, indeed, contemplated at all. The essence of this stage is construction. It is by means of suitable constructions that the great framework of applied mathematics, comprising the theories of number, quantity, time, and space, is elaborated.

It is impossible even in brief outline to explain how mathematics is developed from the concepts of class and correlation, including many-cornered correlations, which are established in the third section. I can only allude to the headings of the process which is fully developed in the work. "Mathematica Principia," by Mr. Russell and myself. There are in this process of development seven special sorts of correlations which are of peculiar interest. The first sort comprises one-to-many, many-to-one, and one-to-one correlations. The second sort comprises serial relations, that is, correlations by which the members of some field are arranged in a serial order, so that, in the sense defined by the relation, any member of the field is either before or after any other member. The third class comprises inductive relations, that is, correlations on which the theory of mathematical induction depends. The fourth class comprises selective relations, which are required for the general theory of arithmetic operations, and elsewhere. It is in connection with such relations that the famous multiplicative axiom arises for consideration. The fifth class comprises vector relations, from which the theory of quantity arises. The sixth class comprises ratio relations, which interconnect number and quantity. The seventh class comprises three-cornered and four-cornered relations which occur in Geometry.

A bare enumeration of technical names, such as the above, is not very illuminating, though it may help to a comprehension of the demarcations of the subject. Please remember that the names are technical names, meant, no doubt, to be suggestive, but used in strictly defined senses. We have suffered much from critics who consider it sufficient to criticise our procedure on the slender basis of a knowledge of the dictionary meanings of such terms. For example, a one-to-one correlation depends on the notion of a class with only one member, and this notion is defined without appeal to the concept of the number one. The notion of diversity is all that is wanted. Thus the class α has only one member, if (1) the class of values of x which satisfies the propositional function,

x is not a member of α,

is not the whole type of relevant values of x, and (2) the propositional function,

x and y are members of α, and x is diverse from y,

is false, whatever be the values of x and y in the relevant type.

Analogous procedures are obviously possible for higher finite cardinal members. Thus, step by step, the whole cycle of current mathematical ideas is capable of logical definition. The process is detailed and laborious, and, like all science, knows nothing of a royal road of airy phrases. The essence of the process is, first to construct the notion in terms of the forms of propositions, that is, in terms of the relevant propositional functions, and secondly to prove the fundamental truths which hold about the notion by reference to the results obtained in the algebraic section of logic.

It will be seen that in this process the whole apparatus of special indefinable mathematical concepts, and special *à priori* mathematical premises, respecting number, quantity, and space, has vanished. Mathematics is merely an apparatus for analysing the deductions which can be drawn from any particular premises, supplied by common sense, or by more refined scientific observation, so far as these deductions depend on the forms of the propositions. Propositions of certain forms are continually occurring in thought. Our existing mathematics is the analysis of deductions, which concern those forms and in some way are important, either from practical utility or theoretical interest. Here I am speaking of the science as it in fact exists. A theoretical definition of mathematics must include in its scope any deductions depending on the mere forms of propositions. But, of course, no one would wish to develop that part of mathematics which in no sense is of importance.

This hasty summary of logical ideas suggests some reflections. The question arises, How many forms of propositions are there? The answer is, an unending number. The reason for the supposed sterility of logical science can thus be discerned. Aristotle founded the science by conceiving the idea of the form of a proposition, and by conceiving deduction as taking place in virtue of the forms. But he confined propositions to four forms, now named A, I, E, O. So long as logicians were obsessed by this unfortunate restriction, real progress was impossible. Again, in their theory of form, both Aristotle and subsequent logicians came very near to the theory of the logical variable. But to come very near to a true theory, and to grasp its precise application, are two very different things, as the history of science teaches us. Everything of importance has been said before by somebody who did not discover it.

Again, one reason why logical deductions are not obvious is that logical form is not a subject which ordinarily enters into thought. Common-sense deduction probably moves by blind instinct from concrete proposition to concrete proposition, guided by some habitual association of ideas. Thus common sense fails in the presence of a wealth of material.

A more important question is the relation of induction, based on observation, to deductive logic. There is a tradition of opposition between adherents of induction and of deduction. In my view, it would be just as sensible for the two ends of a worm to quarrel. Both observation and deduction are necessary for any knowledge worth having. We cannot get at an inductive law without having recourse to a propositional function. For example, take the statement of observed fact,

This body is mercury, and its specific heat is 3·033.

The propositional function is formed,

Either x is not mercury, or its specific heat is 0·033.

The inductive law is the assumption of the truth of the general proposition, that the above propositional function is true for every value of x in the relevant type.

But it is objected that this process and its consequences are so simple that an elaborate science is out of place. In the same way, a British sailor knows the salt sea when he sails over it. What, then, is the use of an elaborate chemical analysis of sea-water? There is the general answer, that you cannot know too much of methods which you always employ; and there is the special answer, that logical forms and logical implications are not so very simple, and that the whole of mathematics is evidence to this effect.

One great use of the study of logical method is not in the region of elaborate deduction, but to guide us in the study of the formation of the main concepts of science. Consider Geometry, for example. What are the points which compose space? Euclid tells us that they are without parts and without magnitude. But how is the notion of a point derived from the sense-perceptions from which science starts? Certainly points are not direct deliverances of the senses. Here and there we may see or unpleasantly feel something suggestive of a point. But this is a rare phenomenon, and certainly does not warrant the conception of space as composed of points. Our knowledge of space properties is not based on any observations of relations between points. It arises from experience of relations between bodies. Now a fundamental space relation between bodies is that one body may be part of another. We are tempted to define the "whole and part" relation by saying that the points occupied by the part are some of the points occupied by the whole. But "whole and part" being more fundamental than the notion of "point," this definition is really circular and vicious.

We accordingly ask whether any other definition of "spatial whole and part" can be given. I think that it can be done in this way, though, if I be mistaken, it is unessential to my general argument. We have come to the conclusion that an extended body is nothing else than the class of perceptions of it by all its percipients, actual or ideal. Of course, it is not any class of perceptions, but a certain definite sort of class which I have not defined here, except by the vicious method of saying that they are perceptions of a body. Now, the perceptions of a part of a body are among the perceptions which compose the whole body. Thus two bodies a and b are both classes of perceptions; and b is part of a when the class which is b is contained in the class which is a. It immediately follows from the logical form of this definition that if b is part of a, and c is part of b, then c is part of a. Thus the relation "whole to part" is transitive. Again, it will be convenient to allow that a body is part of itself. This is a mere question of how you draw the definition. With this understanding, the relation is reflexive. Finally, if a is part of b, and b is part of a, then a and b must be identical. These properties of "whole and part" are not fresh assumptions, they follow from the logical form of our definition.

One assumption has to be made if we assume the ideal infinite divisibility of space. Namely, we assume that every class of perceptions which is an extended body contains other classes of perceptions which are extended bodies diverse from itself. This assumption makes rather a large draft on the theory of ideal perceptions. Geometry vanishes unless in some form you make it. The assumption is not peculiar to my exposition.

It is then possible to define what we mean by a point. A point is the class of extended objects which, in ordinary language, contain that point. The definition, without presupposing the idea of a point, is rather elaborate, and I have not now time for its statement.

The advantage of introducing points into Geometry is the simplicity of the logical expression of their mutual relations. For science, simplicity of definition is of slight importance, but simplicity of mutual relations is essential. Another example of this law is the way physicists and chemists have dissolved the simple idea of an extended body, say of a chair, which a child understands, into a bewildering notion of a complex dance of molecules and atoms and electrons and waves of light. They have thereby gained notions with simpler logical relations.

Space as thus conceived is the exact formulation of the properties of the apparent space of the common-sense world of experience. It is not necessarily the best mode of conceiving the space of the physicist. The one essential requisite is that the correspondence between the common-sense world in its space and the physicists' world in its space should be definite and reciprocal.

I will now break off the exposition of the function of logic in connection with the science of natural phenomena. I have endeavoured to exhibit it as the organising principle, analysing the derivation of the concepts from the immediate phenomena, examining the structure of the general propositions which are the assumed laws of nature, establishing their relations to each other in respect to reciprocal implications, deducing the phenomena we may expect under given circumstances.

Logic, properly used, does not shackle thought. It gives freedom and, above all, boldness. Illogical thought hesitates to draw conclusions, because it never knows either what it means, or what it assumes, or how far it trusts its own assumptions, or what will be the effect of any modification of assumptions. Also the mind untrained in that part of constructive logic which is relevant to the subject in hand will be ignorant of the sort of conclusions which follow from various sorts of assumptions, and will be correspondingly dull in divining the inductive laws. The fundamental training in this relevant logic is, undoubtedly, to ponder with an active mind over the known facts of the case, directly observed. But where elaborate deductions are possible, this mental activity requires for its full exercise the direct study of the abstract logical relations. This is applied mathematics.

Neither logic without observation, nor observation without logic, can move one step in the formation of science. We may conceive humanity as engaged in an internecine conflict between youth and age. Youth is not defined by years, but by the creative impulse to make something. The aged are those who, before all things, desire not to make a mistake. Logic is the olive branch from the old to the young, the wand which in the hands of youth has the magic property of creating science.

SOME ASPECTS OF THE FUTURE OF THE SYNTHETIC CHEMICAL INDUSTRY OF GREAT BRITAIN.*

By FRANCIS H. CARR.

SINCE the outbreak of war we have read and listened to much concerning the question how to assist the development of British chemical industry, and nearly all that we have read and heard as to the need of co-operation in both research and industry, and their systematic organisation in matters financial, manufacturing, and educational, has met with our approval. Over and over again we have been urged to take resolute action—as, indeed, we were, also, from time to time before the war. Already, not a few of us are getting very weary of these discussions and are determined to replace them by immediate action.

What has been said of the British chemical industry in general applies with special force to the synthetic chemical branch, with which I propose to deal. As I wish to refrain, if possible, from the repetition referred to, will you please excuse me from attempting to give any complete survey of the future prospects of this branch and allow me to deal with the educational aspect of the matter, which, after all, may be the one of which you are weariest? It must be because I am not an educationalist that I am bold enough to come before men who are so qualified, and make fresh and heterodox proposals for which a teacher of chemistry might incur severe chastisement at your hands. However, if one may proceed, let it be assumed that we understand approximately the present position of the synthetic chemical industry, and how we have been led during the war to manufacture many dyes and medicinal chemicals in addition to those which were previously made here. Of many of these substances the demand (generally created by Germans) had by that time, and in most cases long previously, become an imperative need. It is equally understood that this great need and the enormous increase in prices resulting therefrom have temporarily opened the way to the manufacture of many dyes and medicinal and photographical chemicals not hitherto made here. Probably we are agreed, also, as to the need of taking steps to protect the industry from destruction by foreign competition during the early years after the war, and as to that of establishing it ultimately without dependence upon any form of protective measures—for, in the long run, scientific efficiency must determine which nation shall retain an industry. What, then, are the conditions required to make the synthetic chemical branch of the industry flourish and expand in Great Britain?

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The manufacture of synthetic chemicals is, perhaps, peculiar among manufactures in one respect. A very great diversity of operations involving expert knowledge has to be carried out in the preparation of any one compound, and, with but few exceptions, the demand for any one such substance is so small that, for economic reasons, its manufacture cannot be carried on continuously all the year round. The diversity of functions required of workers and organisation must therefore be still further extended by the making now of one compound, now of quite a different one. In addition to being various, the operations, as already indicated, are often difficult, requiring skill and experience, lack of which on the part of the workman may entail heavy losses.

We are generally agreed, no doubt, that this diversity makes co-operation between manufacturers a fundamental necessity, so that intermediate products required for several manufactures may be made economically, and therefore on the largest possible scale, and without unnecessary overlapping. But I wish to focus attention upon the type of men required to carry on and direct such manufactures, and to point out that if our educational provisions for supplying suitable men were less haphazard it would be greatly to the advantage of chemical manufacture in Great Britain. At the same time, it must be admitted that the prospects of those embarking on a chemical career are not as alluring as they might or ought to be.

The works chemist is not a greatly envied man as is, say, a medical practitioner, a barrister-at-law, or a civil engineer, yet he should have at least as lengthy an education as any of these. The industry needs more men of ability, character, and courage, and to get them we must improve the position both as regards scientific recognition and remuneration. The latter should be liberal enough, not only to attract men of first-rate ability to the industry, but to retain them on its technical side. It is anomalous that a man's earning capacity should generally be considered distinctly greater in commercial than in technical occupations; the anomaly unfortunately exists, and is responsible for a good many deliberate desertions of the technical for the commercial side of a business. A more general adoption of systems of partial payment by results would not only benefit both employer and employed, but would have far-reaching effects upon the whole industry by stimulating men to greater effort and inducing them to remain at their technical work. Scientifically trained people would do well when accepting engagements to stipulate for some scheme of participation in the fruitfulness of their work. Such schemes have worked well for both parties in the chemical industry on the Continent, and have been a material factor in its progress.

Let it be granted, then, that the chemical industry is in need of specially trained workers—a position which, after all, is true of many industries. By what process ought they to be prepared? In the college, in the factory, or in both? Most of us will agree that it must be by the last-mentioned combination—that neither college nor factory can alone complete the training; but as to the details of the functions to be performed by the two there is greater room for difference of opinion.

At this stage we need to discriminate between two classes of workers, namely (1) technical and scientifically trained departmental managers, and (2) expert operatives. The first class consists of resourceful well-trained chemists actually directing on the spot operatives of the second class. They must be men prepared to give directions when a reaction takes a different course from that expected; men with some engineering as well as chemical training; men who can carefully harvest from daily observations all those deductions which, in sum total, become invaluable knowledge. Such accumulative experience of practical detail is the secret of success, leading yields higher and higher, making the labour cost of the product less and less, and resulting at times in important discoveries. This power of controlling complicated and delicate processes, not merely conscientiously but with intelligence and initiative, of observing closely and of appreciating what in the mass of observed details is of practical as well as of scientific importance, demands qualities of mind and of interest which are different from, though not incompatible with, those of the research chemist in the narrower sense. The industrial chemist may have the research instinct and will not need to starve it, but his hunger after new knowledge for its own sake must not prevent his giving interest and enthusiasm to saving on the cost of materials, labour, and fuel; and such work demands not merely a type of ability as specialised as that of the research chemist, but above all a type of training which our educational system appears most conspicuously to lack. I regard it as fundamental to the solution of the problem before us. For it is in synthetic chemical manufacture above all other branches of chemical manufacture that men of this kind are indispensable, and it is to lack of educational provision for their development and encouragement more than to anything else that I am disposed to attribute our failure in that field.

One needs to apologise, I suppose, for dealing at greater length with this well-worn topic of education, yet I feel compelled to do so by reason of the great need of some means for more quickly and effectively supplementing university education in these respects so as to fit men for the pursuit of industrial chemistry. As we have heard so often, the university graduate, including the B.Sc.Tech., has even less knowledge of how to contrive to apply his knowledge than the manufacturer has of how to utilise it; the result being that the chemist in his caged laboratory is held by his employer at arm's length from manufacturing operations, and his lack of self-confidence still further increases the difficulty of putting his knowledge into practice. The working foreman's rule-of-thumb knowledge—to which great respect is due—is commonly regarded by the manager as a bulwark not to be shaken by any theoretical considerations, however plausibly they may be put forward by the chemist; and experience often justifies this attitude because, although the chemist knows, he does not know that he knows, and he therefore lacks confidence in applying his knowledge. The first failure is regarded as proof of mistake instead of the first stepping-stone to success, which indeed it often is. The trained chemist, without understanding the practical application of knowledge, is in a dilemma in industry—he must either gain knowledge by risking mistakes or remain in insignificance in his laboratory. That is the difficulty; the question is, can we evolve a practical scheme for removing it? The orthodox educationalist view is, I believe, that after the stage of graduation, training can best be carried out either in the research laboratory or in the industrial establishment. My own view is that neither of these places at present affords the proper training required. The shortcomings of the research laboratory for this purpose have been already indicated, and it is self-evident that competitive industrial concerns will not facilitate the training of men either by affording them the necessary leisure or by enabling them to pass from one works to another. It is notorious that in fear of such men passing on secrets (some real, others imaginary) to competing firms, employers put many difficulties in the way of such training as the works might afford, and sometimes metaphorically keep their chemists locked up in the laboratory.

In addition to a sound and thorough fundamental knowledge of chemistry, physics, and engineering, and a little of many other things, the works chemist requires the knowledge of applying knowledge. He needs to understand the business of applying chemistry to manufacture, just as the engineer does the application of physics to the same end. At present we ignore the study of the history of industrial processes, the economics of chemistry, the accountancy of chemistry, and the applied mathematics, mechanics, and engineering of chemistry; yet all of these are subjects capable of being taught to great advantage and for the most part in the laboratory in much the same way as electrical and mechanical engineering are taught. The scheme which I desire to propose applies exclusively to students who have creditably passed through a full college curriculum. It involves the formation of one or more technological colleges of a new type. Such a college would itself be nothing less than a manufacturing concern, having a complete and well regulated course extending over, say, two years, the students of which would spend a considerable portion of their time in actually manufacturing, under the direction of experienced technical men, those inorganic and organic compounds which are required in relatively small quantities by educational and research institutions throughout the Empire. For supplies of these substances we have, to our no small discredit, been dependent almost entirely upon German enterprise, and even, in many instances, on that of one particular German firm. With such productions the ordinary manufacturer will not be troubled, since the demand is so small and irregular as to render them insufficiently remunerative.

The college would need a large permanent staff who would conduct it on lines of strict and complete business organisation and discipline. The hours of attendance would be not less than eight per day and the holidays short. To enforce the regulations, power of dismissal would be given to those in control, and no student would be able to proceed from one stage in his course to another without having qualified in the earlier one.

Structurally, the college would be composed of the lecture rooms, chemical, physical, and engineering laboratories, drawing office, and, in addition, a series of well-equipped manufacturing laboratories, with store-rooms, joiners' and fitters' shops, and so forth, and, lastly, but by no means of least importance, a power plant generating steam, gas, and electricity under such conditions that the efficiency is daily computed and under control. The steam, gas, water, and electricity supplied to each section should be recorded on meters, for the fundamental requirements must be that the student should learn to approach chemical operations quantitatively from the point of view of the value of raw materials, the yield of product, the heat and power absorbed, and time and labour expended.

To assist the student in getting the true commercial perspective he would, in the beginning, attend a course of instruction in accountancy and costing as exemplified in the system adopted throughout the college.

Having said so much of the general idea of my scheme I wish, before entering into other details, to explain that the object in view is not to teach the method of manufacture of a particular product or kind of product. Although this may be done successfully in the case of certain industries, as, for example, brewing and tanning, it is clearly impossible for the chemical industry in general; but the care and exercise of resource required in the manufacture of a selection of chemicals on the small manufacturing scale of from 5 to 1000 kilos. are typical of most manufactures, and instructions on these lines could, I claim, be made of immense value, though, of course, the whole of a manufacturer's knowledge can, by no conceivable means, be given in an institution.

In his progress through the laboratories the student would spend some time during the first year in an analytical department, in which the intermediate and finished products are submitted to examination for purity. It would be the function of the permanent staff of this department to set such a standard of perfection in manufacture as should uphold the reputation of the college with the institutions using its products, and, incidentally in many cases, supplying it with students. Much of the care expended in the works would be determined by the efficiency of this department, and the fact that the reputation of the college would depend on the judgment of those institutions and colleges to which the products are supplied would act effectively in maintaining a standard of excellence of work.

During the first year the student would attend courses of instruction in physical and electro-chemistry, applied mathematics, construction and design, chemical engineering, machine drawing, &c.; he would also receive practical instruction in the repair shop and power-house, as well as in the use of special machinery and plant. He would take his turn at stoking, engine driving, making steam-joints, lead-burning, and so forth.

Passing into the works laboratory, first-year students would be set in small groups to manufacture at first simple inorganic compounds, and would be given an opportunity of watching the operations of advanced students. These manufacturing operations would need to be conducted under strict discipline as regards both time spent and quantitative results, and although from its nature the work would not be on the full scale of ordinary technical procedure, it would be carried out on a sufficiently large scale to require manufacturing apparatus as distinguished from that of the laboratory. During the first and second year, students gradually would become familiar with the construction and use of autoclaves, large reaction vessels, vacuum pans, gas compressors, furnaces, centrifuges, filter-presses, and so forth, and would acquire experience in handling difficult and dangerous substances, in utilising catalysts, &c. He would also have experience in designing special pieces of plant for particular technical processes. In the second year, courses of lectures would include various engineering aspects, among them steam raising and power production, every student spending several weeks in the department concerned with the supply of steam and power to the institution, and in a laboratory in which fuel, water, and flue gases, &c., are analysed.

Courses of instruction in special manufactures, such as sulphuric acid and alkali, would probably find their place in the curriculum; arrangements might be made for students destined for particular industries to attend special courses of instruction given by men actually engaged in the industries in question—a proceeding which has already been adopted in the evening classes of some of our technical colleges.

Further, it would be an invaluable adjunct to such a college if arrangements could be made for students to attend courses of practical instruction in actual works. By careful arrangement this might be done with such slight interference to the business of the firms concerned during only a short period in each year that the opposition to the proposal would be satisfactorily met. Above all, it is essential that the staff of the college should consist mainly of men of ripened works experience—not, be it understood, men (however able) who have merely spent a period in the research or analytical department of a works. Such men have usually been regarded by our educational authorities as men with works experience, when in point of fact they have little more real claim to a knowledge of chemical manufacture than has the average practising analyst.

As regards the nature of the substances manufactured the first-year students would be occupied partly in making from raw material simple inorganic substances; for instance, potassium bichromate and permanganate, metallic arsenic and tellurium, hydrogen peroxide, hydriodic acid and ammonium persulphate, and partly in isolating and purifying tar products, sugars, and natural vegetable products, such as theobromine and caffeine.

In the second and succeeding years—for it may be safely assumed that many students would remain longer than two years, and it should prove possible to pay them small salaries to do so—the students would be occupied in carrying out synthetic organic processes on the large scale; they would be enabled to follow each other's processes, being present to watch critical stages and so enlarging their experience.

The compounds manufactured would, in general, be those which, while not in common use, are required for exceptional purposes, chiefly by colleges and research laboratories. In order that the scale may be a large one it would be necessary to make of many substances much bigger quantities than are likely to be required; these might remain in storage for many years, and only gradually would a complete list of the substances in demand be accumulated.

One claim for this scheme is, that besides affording a really practical training, it would maintain and impart by means of actual manufacture and sales a standard of industrial efficiency almost impossible of attainment without this incentive. It would also have the further practical value of supplying many chemicals for which we have hitherto been dependent upon Germany. Nor need we fear that such a scheme would give serious offence in commercial quarters, for the monetary value of business in the manufacture of fine chemicals of this type is of no great account, snd it would not be difficult to avoid jealousies by confining the manufacture to those substances which manufacturers of fine chemicals do not wish to produce.

If a manufacturer should complain that he is subjected to unfair competition through the production of a certain chemical by an endowed and privileged institution the reply is simple: let him produce a supply of the substance of adequate purity, and it may be assumed that the college of my conception would leave it to him.

Incidentally, the college would prove of great advantage to research workers, who would have here facilities for procuring the compounds with which their investigation commences, instead of spending a lot of their valuable time in repeating tedious preparations on a small scale. This single benefit, increasing as it would the effectiveness of research workers, would react favourably on the industry as a whole.

It may be objected that by the time a student has graduated he has no means to continue his education for two more years, making the course, say, five years in all. If we consider the number of medical students who find the means for a course of usually greater length the difficulty does not appear insuperable. It may be met to some extent by the suggestion that no student in this college should proceed to his second year unless he merits promotion by his attendance and progress in the first year; it might then be possible to remit the fees in the second year, or even to give a small remuneration. The sales of the chemist's products would, perhaps, assist partly in enabling this to be done, but endowment by the Government as well as by the Association of British Chemical Manufacturers should do so more materially.

Chemical manufacturers commonly pay salaries to members of their staff who are trying to teach themselves what might be more quickly taught in the institution I have sketched, but still more must be spent for this purpose if our industry is to progress, and it would be far more economical to do so in the manner here proposed. No doubt can exist that contributions from employers through the Association of Chemical Manufacturers might afford a substantial and adequate endowment, but for the cost of the buildings and equipment surely we might justly look to the Government, for it is recognised in the highest quarters that our educational organisation must be directed to practical ends of this very nature.

Dealing next with the training of the expert operative, we recognise that his chief training ground is now the factory, and must remain so for the present. Unfortunately, the lack of an established apprenticeship system in the chemical trade renders this training very uncertain and at times valueless, and efforts are needed to improve it. Much may be done by utilising the research and analytical laboratories of a works for the purpose of training selected boys from primary and secondary schools. To secure the success of such a method attendance at evening classes should be a condition of engagement in these laboratories, and the fees ought to be paid by the employer. This plan has many limitations, for not only may it be disadvantageous to the work of the laboratories to pass youths forward in this way, but the amount of attention which can be given to them is insufficient, and the number so trained does not meet the requirements of a growing industry. Our secondary schools, excellent though many of them are, fail lamentably to produce youths suitable for industrial careers. Too little latitude is granted by the Board of Education to permit of youths in a particular district being trained for industries belonging thereto, nor is there sufficient differentiation at the age of about thirteen in the training given to boys of quite different aptitudes. It would not be difficult in large towns to arrange that one or other institution should frame its course somewhat on the line of the old Mechanics' Institute, whose discontinuance has proved such a real loss—selecting the boys who are to attend it from all the other secondary schools of the district. The selection would be comparable to that which at present is made in the case of students proceeding to the commercial course in some secondary schools. Physics, mechanics, chemistry, mathematics, machine construction, and mechanical drawing should figure on the time-table, and the full course would extend to four years.

In addition to this modification of our secondary schools one cannot plead too often or too much for the Government of this country immediately to adopt compulsory continuation of the education of those brought up in our primary schools; at least eight hours per week should be so spent until eighteen years of age, the hours which people of this age can be employed in factories being limited to forty per week, and the secondary schools, already referred to, supplying the necessary classes. But this is not the proper occasion for discussing in detail the large question of general primary and secondary education. It suffices here to call attention to the fact that chemical manufacture among many other industries would be greatly benefited by the reforms referred to.

No mention has been made of the educational provision for training research workers, because it is felt that our universities are capable of turning out all that we require, Of their capacity in this respect as well as of the competency of British students we may rest well assured. Of greater moment is it that manufacturers should understand the commercial value of pure research, and that they should, both by co-operating with the universities and by providing their own laboratories, render it possible for these researchers to carry on their investigations.

To look upon research as a business proposition has been distasteful to many of that great band of devotees to science who have been attracted thereto by the love of research and the quest of knowledge for its own sake, but I am sure it would be healthful if this attitude on the part of scientific men were somewhat modified so that matters of practical importance might, without prejudice to scientific reputation, frequently form the subject of research in academic laboratories and of theses for degrees.

The commercial exploitation of the results of researches is a matter calling for careful attention in this country in the domain of medicinal chemistry. This matter presents considerable difficulty, partly because the medical fraternity are very conservative and unwilling to adopt new remedies, but mainly because of the difficulty in getting drugs tested and getting official recognition of their utility. In Germany the demand for such new remedies has been created by medical men rewarded for their services, a system happily impossible in this country and one which may do damage to the health of the unfortunate consumers. To overcome these difficulties it is suggested that institutions, universities, and hospitals should co-operate in performing physiological and chemical tests of likely substances, and that some body such, for instance, as the Medical Research Committee should, on examination and confirmation of the evidence thus afforded, authoritatively express opinion on the usefulness of new drugs, which opinion, properly vouched for in this way, would no doubt be accepted by the medical practitioners. This is particularly difficult under the present system by which good and bad remedies alike become known to them by the advertisements of interested firms.

In conclusion, let me reiterate in a very few words what I have endeavoured to express at greater length in this paper, namely, that the future of synthetic chemical manufacture as well as of other branches of the industry in this country can only be secured by greater progress in organisation and by co-operation among the various firms engaged in it. That, in addition, there must be an important development in our system of technical education so as to increase the efficiency of labour and its scientific management. For this purpose I have put forward with all modesty certain practical suggestions.

Finally, let us not wander like the Lost Tribes of Israel in the Desert, crying aloud to the Government to act as our Providence, but let us continue to work out our own salvation, and trust the Government to give the assistance we need when we ask for it.

THE DETECTION OF NATURAL AND ARTIFICIAL PIGMENTS IN OLEOMARGARINE AND BUTTER.*

By LEROY S. PALMER AND WALTER E. THRUN.

(Concluded from p. 136).

Moore's Test (continued).

Carotin is an unsaturated hydrocarbon and loses its colour on oxidation. Dissolved in fat, however, it is very stable towards all the ordinary laboratory reagents, such as most metallic salts, alkalis, dilute acids, both mineral and organic, and glacial acetic acid. That it should be decolorised so readily in Moore's test through the agency of the ferric chloride seemed worthy of more extended study. Numerous tests on samples of butter fat with a natural yellow colour showed that the decolorisation of the carotin could be brought about much more readily if a better contact was secured between the carotin and the ferric chloride than is given by Moore's test. For example, one or two drops of 1 per cent aqueous ferric chloride solution added to a solution of 5 cc. of fat in 25 cc. of hot absolute alcohol caused an almost instantaneous decolorisation of the fat, which separated colourless when the alcohol cooled, or if sufficient water was added to cause the separation to take place. Especially striking, however, was the reaction which was found to take place when a very small crystal of pure ferric chloride was added directly to 5 cc. of hot melted fat. On shaking, the ferric chloride dissolved in the fat and the yellow colour was rapidly replaced by a beautiful green colour. When the fat was shaken with 10 cc of methyl or 95 per cent ethyl alcohol the green colour was extracted and the fat was found to have been completely decolorised. If more ferric chloride was added than necessary to decolorise the fat the green colour did not appear; instead the fat remained yellow, due to the excess ferric chloride in solution. On extracting this with alcohol the fat was found to have been decolorised, the ferric chloride going into the alcohol layer and the fat separating colourless.

The green coloration seen in the above test was found to be due to the ferrous chloride formed from the ferric chloride by the reducing action of the carotin, the carotin at the same time being oxidised and decolorised. Ferrous chloride solutions are characterised by their green colour, as is well known. Husemann (*loc. cit.*, 226) first pointed out that carotin has an action on ferric chloride when he recorded his observation that "Eisenchloride erteilt der weingeistigen Losung eine bei auffallendum Lichte grünlich erscheinende dunklere Färbung." He obviously overlooked the decolorisation of the carotin in the test, and also that alcohol itself reduces ferric chloride, methyl alcohol solutions being especially characterised by their green colour. We have found that the reduction of ferric chloride to ferrous chloride by carotin may be strikingly shown by dropping a crystal of the ferric salt on a freshly prepared amorphous residue from the chloroform extract of carrot pulp. The ferric chloride turns a beautiful green, and the aqueous solution of the reduced iron salt gives a strong test for ferrous ions on addition of potassium ferricyanide, care being taken that the ferric chloride used alone shows no precipitate of "Turnbull's blue" on addition of the ferricyanide. The yellow carotin residue, to which the ferric chloride is added, is seen to be colourless when the ferrous chloride is washed off with water, in which carotin is insoluble.

With Moore's tests so greatly simplified and the basis of the reaction established, attention was directed to showing whether carotin added artificially to fat would act differently from the carotin natural to fat. For this purpose butter fat naturally nearly free from carotin and rendered fat from white oleomargarine were coloured by warming the melted fat with carrot pulp, with frequent shaking. (Some carrots were peeled, ground up, and boiled with water. The pulp was pressed, dried, ground up as finely as possible, and used for colouring the fat). The yellow fats prepared in this way, together with freshly rendered Jersey-cow body-fat, which had a high natural yellow colour, were subjected to Martin's test, to Moore's test as given by Leach, and also to the several modifications of this test mentioned above. Identical results were secured in each test with all the fats. Martin's test failed to extract the carotin, but the ferric chloride caused a decolorisation in all the tests in which its use was involved. The green coloration of the fat, when just sufficient ferric chloride was added directly to the fat to cause the oxidation of the carotin, was just as striking in the cases of added carotin as in the cases of the fats naturally coloured by this colouring matter. The conclusion drawn from these results was that it is not possible to differentiate by this method between the carotin natural to butter fat and beef tallow (oleomargarine) and carotin that has been added artificially to these fats.

It was found possible, however, to detect the presence of both carotin and other pigments, such as annatto, when present in the same fat. This is due to the fact that annatto and all other pigments not natural to fat can be practically quantitatively extracted from fat by Martin's method if the fat is shaken with several successive portions of Martin's reagent. Several tests of this character were made, and it was found that when the extract was no longer coloured in Martin's test any colouring matter that remained in the fat could be readily identified as carotin by the modified Moore's test. Annatto, which belongs to the same class of vegetable pigments as carotin, was also found to be decolorised by ferric chloride. When dissolved in fat, however, its oxidation was not found to be as rapid as that of carotin. The very fact that it does respond to the same test, however, makes its extraction from the fat by Martin's or some other reagent necessary before testing for the presence of carotin.

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* From *Journal of Industrial and Engineering Chemistry*, viii., No. 7.

Author's Test.

The following method, summarising what has been given above, is recommended for the detection of artificial and natural (carotin) pigments in butter fat and oleomargarine.

Shake 10 cc. of rendered, melted fat with successive 25 cc. portions of Martin's reagent (15 parts 95 per cent alcohol and 2 parts carbon disulphide) until no more colour is extracted. Test the extracted colouring matter for annatto or other pigments by one or more of the approved methods. Drain off *all* of the alcohol from the fat, and test the pigment remaining in the fat for carotin by adding a small crystal of pure ferric chloride to the hot melted fat. After thorough shaking extract with 10 cc. of methyl or 95 per cent ethyl alcohol. If the pigment was carotin the fat which separates will when melted be seen to be completely decolorised. If just sufficient ferric chloride is added to cause complete decolorisation the ferrous chloride formed will impart a beautiful green colour to the fat.

Discussion.

One of the most interesting results of this brief study is the impossibility of differentiating between the natural yellow colouring matter of butter fat and beef tallow and the same colouring matter added artificially to these fats. The conclusion that would naturally be drawn from this result is that the carotin of butter fat and beef fat exists there in simple solution. The question of how this pigment exists in animal fats was not investigated in the studies of the general question of yellow animal pigments recently published by one of us (Leroy S. Palmer and C. H. Eckles, *loc. cit.*). The assumption was that a simple solution of the pigments existed in the fats. That assumption seems to be substantiated by the tests made in the present study.

Mention of the fact that the carotin natural to butter fat and beef fat has a small amount of xanthophyl associated with it has been purposely avoided throughout the paper for fear of confusing the main problem. Although xanthophyl is abundant in all vegetable matter containing carotin, it comprises such a small proportion of the total colouring matter of butter fat and beef fat, even under the most favourable conditions, that it can be practically left out of consideration. Moreover, xanthophyl appears to be as completely decolorised by ferric chloride as carotin. The existence of xanthophyl to an appreciable extent in carrots and the ready solubility of xanthophyl in fat makes it reasonably certain that it was present in the fat in the cases of artificial coloration with carotin, in which as complete oxidation of the pigments by the ferric chloride resulted as in the cases involving the natural pigment only.

From the viewpoint of the analyst it is unfortunate that it does not appear possible to detect the presence of carotin added artificially to butter fat or oleomargarine. This conclusion may be a hasty one, however. Although it will probably never be possible to differentiate between natural and added carotin in fats, it may be possible, should the food laws ever require it, to tell whether carotin has been added to fat. While no attempt has been made to work out any tests in this connection, it is suggested that the possibilities of determining whether carotin has been added lie in the fact that xanthophyl is naturally present in animal fats in very small proportion of the total pigment, while it is present in much greater proportion in all the vegetable matter containing carotin which might be used as a source of carotin for the artificial coloration of fat; furthermore, it would not be possible to extract the carotin from these sources without at the same time extracting the xanthophyl. Accordingly butter fat or oleomargarine containing added carotin would likewise contain a much greater proportion of xanthophyl than is natural to these fats. It is doubtful if any simple test can be devised for determining the relative proportion of carotin and xanthophyl in fat. The solution of the problem would probably have to involve a separation of the total pigment from the fat and a subsequent separation of the extracted pigment into its carotin and xanthophyl portions by means of one of the relative solubility properties of these two classes of pigments. These properties are discussed fully in the studies on animal pigments previously published from the Dairy Chemistry Laboratory, University of Missouri, Columbia. As the question is not one of immediate moment the reader interested in the question is referred to the publications mentioned.

The strong reducing action of carotin on ferric chloride, which is the basis of the method for the detection of carotin, suggested that other reducible ferric salts might be similarly affected, and accordingly serve equally well for the detection of carotin. This was found to be the case. Ferric nitrate was found to oxidise and decolorise carotin in butter fat, but the test using this salt could not be simplified, as in the case of ferric chloride, owing to the insolubility of ferric nitrate in fat. It was found necessary to add some reagent which would dissolve both the fat and the ferric nitrate, such as acetone. No green coloration accompanied the decolorisation of the carotin in this test, but instead there was a suspension of a reddish brown iron oxide formed from the ferric nitrate.

Summary.

1. It is pointed out that the detection of carotin (the natural yellow pigment of animal fats) in oleomargarine is made necessary by the oleomargarine laws of many States.
2. Cornelison's test for carotin artificially added to fat is shown to be quoted wrongly in Leach's "Food Inspection and Analysis."
3. The relation between Martin's test for artificial pigments in fats and Moore's test for carotin added artificially to fat, as given in Leach's "Food Inspection and Analysis," is shown to be confused, and the true relation is pointed out.
4. It is shown that Moore's test for carotin in fat or oleomargarine is not alone specific for carotin added artificially, but is equally specific for the carotin natural to animal fats.
5. It is shown that the carotin is not dissolved out of the fat in Moore's test, as stated by Moore, but is merely decolorised by the ferric chloride added. The reaction involved is shown to be a reduction of the iron and the simultaneous oxidation of the carotin.
6. Modification and improvements in Moore's tests are given. A method is also suggested for detecting both natural and artificial pigments (other than carotin) in the same fat.
7. The relation of Moore's test to the question of the natural state of carotin in fat, and the possibility of determining whether carotin has been added to butter fat or oleomargarine, are discussed.

Municipal School of Technology, Manchester.—We have received the prospectus of University Courses in this institution for the Session 1916-1917. It contains full information relating to fees and general regulations. The syllabuses of the classes are also given, and the complete time-table, together with descriptions of the laboratories and their equipment and of the buildings generally. The work of the school includes advanced study and research in various branches of science and technology, University courses in the Faculty of Technology, leading to degrees and certificates in all branches of engineering, applied chemistry, textile industries, architecture, and mining; part time day courses and part time evening courses. Separate departmental prospectuses of the part time courses are issued, and may be obtained free on application to the Registrar of the School of Technology.

NOTICES OF BOOKS.

The Nation of the Future. By L. Haden Guest, M.R.C.S.,Eng., L.R.C.P.,Lond. London: G. Bell and Sons, Ltd. 1916. Pp. 115. Price 2s. net.

This "Survey of hygienic conditions and possibilities in school and home life" should be in the hands of all school managers and head teachers in our elementary schools and of those who are interested in the study of social questions. It contains a full description of methods of medically inspecting school-children, explaining the best methods of making reports and keeping records, and goes fully into the question of the work of school clinics. All the papers which form the book were written before the war, and had been published separately in various journals. The author has some very valuable observations to make upon mental and emotional inspection, and writes sanely and most sympathetically upon the subject of providing the right environment, moral as well as physical, for the young. The illustrations are reproductions of photographs which show various different stages of the medical examinations, and classes and games and occupations in special schools.

The Data of Geochemistry. By Frank Wigglesworth Clarke. Third Edition. Washington: Government Printing Office. 1916. Pp. 821.

This bulletin contains a very comprehensive account of the data of geochemistry, especially the vast accumulation of material relating to the American continent. The many unsolved problems of the subject are formulated, and suggestions are made regarding the solution of some of them, and full details are given of the results which have been obtained by the application of the principles and methods of physical chemistry to geology. The bulletin is to be regarded as a summary of, and a guide to, the very abundant literature of geochemistry, and as such will be of real practical value to students, prospectors, and mining engineers. The data relating to the analysis of the waters of the ocean, lakes and rivers, springs and wells are very full, and the composition of the rock forming minerals, the nature of the rocks of the earth's crust, and the decomposition of them are treated in much detail. The third edition of the bulletin, which is an excellent example of the valuable monographs which are issued by the Bureau of Mines, has been considerably enlarged and carefully revised in accordance with the results of recent research.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Newcastle-on-Tyne Meeting of the British Association:—

President—Prof. G. G. Henderson, D.Sc., LL.D., F.R.S.

Vice-Presidents—Prof. W. A. Bone, D.Sc., F.R.S.; J. T. Dunn, D.Sc.; J. E. Stead, D.Sc., F.R.S.

Secretaries—A. Holt, D.Sc. (Recorder); C. H. Desch, D.Sc.; Prof. R. Robinson, D.Sc.; J. A. Smythe, Ph.D., D.Sc.

Committee—Dr. E. F. Armstrong; Dr. P. P. Bedson; Dr. H. Borns; F. H. Carr; Dr. F. D. Chattaway, F.R.S.; Prof. H. B. Dixon, F.R.S.: Prof. A. Findlay; E. F. Hooper; D. T. Jones; Prof. W. C. McC. Lewis; Prof. H. Louis; Prof. T. S. Moore; H. Peile; W. Rintoul; Dr. N. V. Sidgwick; W. Thomson; Dr. W. G. S. Turner; C. M. Whittaker; H. James Yates.

The Papers brought before the Section were as follows:—

Prof. G. G. Henderson—Presidential Address.
Mr. F. H. Carr—Some Aspects of the Future of the Synthetic Chemical Industry of Great Britain.
Mr. C. M. Whittaker—The British Coal-tar Colour Industry in Peace and War.
Mr. W. Rintoul—The Preparation of Chemicals for Laboratory Use.
Joint Discussion with Section C, on the investigation of the chemical and microscopical characters of different varieties of coal, with a view to their most effective utilisation as fuel, and to the extraction of by products.
Dr. P. Phillips Bedson—Description and Exhibition of an Apparatus for Grinding Coal *in vacuo*.
Dr. J. E. Stead, F.R.S.—
(*a*) On the Oxidation of Nickel Steel.
(*b*) On the Reduction of Solid Nickel and Copper Oxides by Solid Iron.
(*c*) On the Disruptive Effect of Carbon Monoxides at 400° to 500° C. on Wrought Iron.
Dr. J. A. Smythe—A Modified Chlorination Process.
Prof. W. M. Thornton—The Stepped Ignition of Gases.
Report of Research Committees—
(*a*) Dynamic Isomerism.
(*b*) The Transformation of Aromatic Nitroamines.
(*c*) The Study of Plant Enzymes.
(*d*) Correlation of Crystalline Form with Molecular Structure.
(*e*) Study of Solubility Phenomena.
(*f*) The Influence of Weather Conditions upon the Amounts of Nitrogen Acids in the Rainfall and the Atmosphere.
(*g*) Non-aromatic Diazonium Salts.
(*h*) Botanical and Chemical Characters of the Eucalypts.
(*i*) Absorption Spectra and Chemical Constitution of Organic Compounds.
(*k*) Hydro-aromatic Substances.
(*l*) Chemical Investigation of Natural Plant Products of Victoria.
(*m*) Research on the Utilisation of Brown Coal By-products.
(*n*) Fuel Economy, Utilisation of Coal, Smoke Prevention.
Joint Discussion with Section G, on the Report of the Committee on Fuel Enonomy, Utilisation of Coal, and Smoke Prevention.

British Industries Fair (Glasgow), 1917.—The Corporation of Glasgow, fully realising the importance of assisting manufacturers and merchants in this Trade Campaign, have decided to organise a British Industries Fair in Glasgow, the objects being, viz.:—

1. To induce British Manufacturers to extend their respective spheres of activity, so that all classes of articles hitherto imported will, so far as possible, henceforth be made at home.
2. To encourage British Merchants to buy their supplies in home markets.
3. To bring Home, Colonial, and Foreign Buyers into touch with British Manufacturers.

With this object in view the Board of Trade, through their Commercial Intelligence Branch, organised two British Industries Fairs in London in 1915 and 1916 These were undoubted successes, showing in a very remarkable way how British manufacturers were able to compete successfully in many articles which it was hitherto supposed they were quite unable to supply to advantage. The Third British Industries Fair organised by the Board of Trade will be held in London from February 26 till March 9, and at their request the Corporation of Glasgow have decided to hold their British Industries Fair at the same time; certain trades being allocated and confined to each centre. The Board of Trade have undertaken to bring the Glasgow Fair to the notice of Oversea Buyers through H.M. Consuls and Trade Commissioners at the same time as announcements regarding the London British Industries Fair are issued. A Central Bureau will be opened in the Fair, for the purpose of introducing the manufacturer to the buyer and the buyer to the manufacturer. Space will be available for the display of goods manufactured by United Kingdom and Colonial firms. Space will be let to exhibitors at very moderate rates, which, to ensure uniformity of design, will include the cost of erection of stands, thereby saving trouble and expense to exhibitors. Further particulars obtainable from the Exhibition Offices, 38, Bath Street, Glasgow, and the Board of Trade, 32, Cheapside, London, E.C.

Northampton Polytechnic Institute.—*Memorandum of New Developments.*—Notwithstanding the disturbance caused by the war the equipment of the various departments was extended during the Session 1914-15 in several directions. In the Mechanical Engineering Department the testing equipment was increased by the addition of a Heenan and Froude dynamometer and the prime mover equipment by a semi-Diesel engine. In the Electrical Engineering Department various transformers and motors of special types were added, and a Tirrell regulator and a mercury arc rectifier were installed. The instrument equipment was also extended, the individual items being too numerous to mention separately. In the Technical Optics and other departments a fair amount was also spent on extensions during the Session 1914-15. The programme of work for the new Session has necessarily been given very careful consideration by the Governing Body, and, speaking generally, it has been decided to continue to announce the various regular classes which have been announced in previous sessions. The courses in the Engineering Day College are to be continued, but the second and third year courses which ordinarily extend from September to Easter are, in 1915-16, to commence in January and to be continued until July. This will enable the students to work up to Christmas in the munitions workshop, which has been fully employed in making gauges and parts of armaments during the whole of the summer vacation. In the evening classes in Engineering it has been found impossible, in the Session 1915-16, to arrange for special series of advanced lectures which have been features of recent sessions, as the possible lecturers who have been approached are all fully engaged in work connected, directly or indirectly, with the war. The only new class, therefore, appearing in the "Announcements" is a "Glass Workers" evening course which is being jointly undertaken by the Technical Optics and the Technical Chemistry Departments. The class is urgently required at the present time owing to the disturbance in this particular trade caused by the war. The special classes for Post Office workmen and boy messengers, started two years ago, are being continued, as are also the classes in Submarine Cable Work for the employees of the various cable companies who have their headquarters in London. The elementary and advanced classes in Radio-Telegraphy are also being announced. In all the departments, including Civil and Mechanical Engineering, Electrical Engineering, Technical Optics, Technical Chemistry, Horology, and Women's Trades, the programmes of the various classes have been brought up to date.

The Swedish Year Book for 1915 contains the ninth annual report of the Council of the Swedish Chamber of Commerce for the United Kingdom and the Transactions of the year 1915. Lengthy trade reports are also included, and articles on finance in 1915, Swedish shipping during the war, and Swedish newspaper advertising during the war. The Year Book comprises over 200 pages of valuable information relating to our trade with Sweden, and should be in the hands of all who are or hope to be in business relations with that country. It is furnished with some excellent maps, and contains a great number of advertisements of Swedish firms.

The Russian Press.—Messrs. Neyroud and Sons, Ltd., of Regent House, Kingsway, W.C., have recently issued a useful little booklet "The Russian Press" which contains a list of the most important Russisn newspapers, periodicals, and trade journals. It is a remarkable fact that while the neutral nations have shown great enterprise in advertising in the Russian press, and thus filling up the gap left owing to the absence of German advertisements (which were very numerous before the war), Great Britain has exhibited the greatest apathy, and has made no attempt to take advantage of the opportunity of pushing her trade. To help to remedy this disastrous state of affairs Messrs. Neyroud and Sons, Ltd., have issued this list, which will give a good idea of the importance of the Russian press and of the services they can render in connection with the development of trade with Russia. They are prepared to send specimen copies of any of the publications, with advertising rates, and will also receive advertisements and put merchants in touch with trustworthy agents.

A Pen's Proud Record.—Not a day passes without some more or less striking testimony to the usefulness and durability of the "Swan" Fountain Pen. The following, however, is a singular and almost unique instance, for surely it is a rare thing for a nib to be split in two and yet continue to give good service. Mr. W. J. Collen-Jones, of East Sheen, writes July, 1916:—"The 'Swan' with which I am writing this letter has served me for over seventeen years without the least trouble or expense, and still goes well, notwithstanding the fact that a year ago I trod on it, smashing the cap and a piece out of the nib-holder and *splitting the nib into two separate halves.* Thanks to the style of feed-controller, I had little difficulty in wedging the broken nib in position, so that it still continues in daily use—often for ten or twelve hours actual writing in a day." Our readers should send for a free Booklet about the "Swan" to the manufacturers, Mabie, Todd, and Co., Ltd., 79 and 80, High Holborn, London, W.C.

TO comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged in Government work will be engaged."

Chemist wanted for large Food Manufacturing Works. Ineligible for Army. Night work necessary at intervals. —Address, "F. 32," Birchall's Advertising Agency, Liverpool.

Chemist (40), married, experienced in fine Tar and Wood Products, Alcohols, Ethers, Sugar, Acids, Explosives, and several Synthetic Products, seeks Engagement. Can design, erect, and start new Chemical Works. English, Continental, and American experience. Willing to go abroad.—Address, "C 40," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Dispenser and Book-keeper required. Married man, to reside at Surgery. Working-class suburb. Wife to act as Housekeeper.—Write, "Doctor," care of W. A. Jennings, 152, Kentish Town Road, N.W.

Wanted for the Association of British Chemical Manufacturers, nn experienced Clerk, who would also act as personal assistant to the General Secretary. Previous experience in a Chemical Broker's office or other knowledge of the Chemical trade desirable. Salary £300 per annum.—Apply to Sir Charles Bedford, 166, Piccadilly, London, W., on Tuesday, 26th inst., at 11 a.m.

FOR SALE.—German Dyes and Intermediate Products, in specimen bottles (2 to 4 ozs.). Also German Chemicals, Porcelain, and Glass Apparatus. All in perfect condition. —Address, "F.I.C.," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

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THE CHEMICAL NEWS

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ADDRESS TO THE ENGINEERING SECTION OF THE BRITISH ASSOCIATION.

Newcastle-on-Tyne, 1916.

By GERALD STONEY, B.A.I. (Dub.), F.R.S., M.Inst.C.E., President of the Section.

At times such as these the mind naturally turns to problems to be considered both at the present time and after the war, and in considering such problems a review of some of the errors committed in the past is most necessary.

Such a review enables methods which should be adopted both now and in the future to be considered.

As this is an address to the Engineering Section of the British Association for the Advancement of Science, only such problems will be considered as affect engineering and its allied industries.

One thing which has handicapped our industries is the reluctance of firms to utilise highly educated labour or to adopt scientific methods. In looking round the industries of the district one is struck by the small number of men who have undergone a thorough scientific training at one of the universities or at one of the leading technical colleges, and who occupy a prominent place in the firms in this district.

The general complaint is that university and college men are too theoretical and not practical.

It is the usual thing for a bad workman to blame his tools, and is it not because employers do not know how to make use of such labour that they utilise it to such a small and imperfect extent?

Things are very different in some other countries with which we have competed in the past, and with which there will be in all probability still fiercer competition in the future. There we find the fullest use made of highly educated scientific labour.

How many engineering firms in this district have a skilled chemist on their staff, and what percentage of these pay him a decent salary? And how many heads of firms have sufficient chemical knowledge to appreciate the work of and utilise the services of such a man, because unless there is appreciation of the work done by such a man his services are useless and he becomes discouraged, generally finding himself up against the blank stone wall of there being no appreciation of his services, and yet chemical problems are continually cropping up in engineering work. There is the question of the supply of materials; as a rule the manufacturer trusts to the name of the contractor and assumes that he gets materials of the composition and purity he ordered. Every now and then something goes wrong and the question arises, why? Without a chemist to analyse the material it is often most difficult to say. Apart from this question of the analysis of raw or partly manufactured materials received, there is the chronic question as to the mixtures of the metals in both the metal and brass foundry, and large economies can be effected by systematic analyses.

Another direction in which scientific labour is invaluable is in seeing that instruments are in proper order and that tests are accurately carried out. Tests carried out with inaccurate instruments and without proper scientific precautions to see that they are accurate and reliable are worse than useless, and in fact most misleading and dangerous, as entirely unreliable inferences may be drawn from them and far-reaching troubles caused in the future. How many tests of steam engines are unreliable because there is no standardisation of the pressure and vacuum gauges snd thermometers used, and in how many cases is even the reading of the barometer omitted? An absolute pressure stated as so many inches of vacuum has no meaning unless the barometer reading is also given or the inches of vacuum is stated as reduced to "Bar. 30." How many firms using steam have any arrangements for testing vacuum and pressure gauges, and yet there are no instruments more liable to error than these gauges? When one tries to analyse the results of steam tests one is constantly up against the elementary question, "Were the gauges, &c., accurate? What a misfortune it is that there were no means of testing their accuracy." Under scientific supervision arrangements are made to avoid such troubles and get reliable results which can be depended on for future designs.

What has been said about pressure gauges and the measurement of pressure applies, of course, to all other instrumente and measurements. In most works, it may be said with sorrow, that the only moderately accurate measurements that can be made are those of dimensions and weight. It is only by accurate testing of existing plant that reliable deductions can be drawn enabling safe progress to be made in future designs.

One of the great things which helped forward the steam turbine in the early days was accurate and full testing of each plant as soon as it was completed and before it left the works. The late Mr. Willans was probably the first, or one of the first, to recognise the importance of accurate testing of steam plant, and the success his well-known engine had was largely due to this. From the earliest days of the steam turbine Sir Charles Parsons recognised the necessity of such testing, and the test-house has always been a prominent feature of Heaton Works. And then in the higher ranks of an engineering works it requires a scientific mind to draw safe conclusions from tests carried out and to see in what directions progress can be safely made. Such methods have enabled the steam turbine during the writer's acquaintance with it, now extending over some twenty-eight years, to grow from 50 horse-power to some 45,000 or more in each unit, and the steam consumption to be reduced from 40 lbs. per h.p. hour to about 7½ lbs., or less than one-fifth.

And closely allied to such work in engineering works is the general question of scientific research, and here a trained scientific mind is of the utmost importance to see that reliable results are obtained and to make true logical deductions from those results. Without suitable training a man is liable to be unable to grasp all the conditions of an experiment and to make deductions from the data obtained which are totally unjustified and often lead to most disastrous results in the future.

Such research is generally carried out in four places—engineering works, private laboratories, engineering colleges, and national laboratories.

The first has already been dealt with.

The second is of comparatively small importance in practice.

As regards the third a great deal of good work has been done in engineering colleges, often under great difficulties for want of plant and money, and it is greatly to the credit of our professors and others that they have succeeded in doing so much with the very inadequate appliances at their disposal, and handicapped for want of funds. How inadequate their income is can be understood when it is remembered that Leipzig University alone has an annual income from the German Government of £100,000, as against a total Government grant to *all* the universities here of about £45,000, or less than half.

Of national laboratories we have only one, the National Physical Laboratory at Teddington, and here again the support given to it is totally inadequate. The total income from all sources last year was only £40,000, and of this £23,000 was charges for work done, such as testing meters and other instruments and such commercial work; the Government grant is only £7000 a year, and besides this £7500 was received for experiments in connection with aeronautics, which is really war work. The balance was made up of subscriptions, grants from technical societies, and miscellaneous receipts. Compare this with the German equivalent, the Reichsanstalt of Berlin, which has an income of £70,000 a year from the Government, or ten times that given to our N.P.L. The Bureau of Standards, the similar institution in U.S.A., has a Government grant of £140,000, or twenty times ours. In the Civil Service Estimates there is an allowance of £40,000 for research, an increase of £15,000 over that allotted last year. The total Estimates are over £20,000,000, so that less than one-fifth per cent is allotted to research.

It is difficult to realise what benefits might be gained by investigations which could be carried on by the N.P.L. if only sufficient funds were available, and of what importance they might be to industry at large. One example may suffice. Some time ago the Reichsanstalt carried out a most complete set of tests on a certain class of machine, an investigation which must have cost several thousands of pounds sterling, apart from the time it occupied. The results of this investigation are available to German manufacturers of this machine, and just before the war preparations were being made to take advantage of this, and from figures stated a large extra economy was expected. This, of course, would enable them, provided the cost of manufacture was not too high, to have an enormous advantage over such machines manufactured without this special knowledge. The Institution of Mechanical Engineers saw the importance of this problem and appointed a Research Committee to deal with the question, but the first question met with is that of finance. Should this be the case in a wealthy country such as this that depends on its manufactures for its very existence? And that such an investigation is required is obvious from the fact that the designs of no two independent manufacturers of this machine in this country agree among themselves. Of course, each claims his is the best, but this cannot be so.

Investigations in engineering shops do not meet such a case. The question of finance has to be carefully watched, and as soon as results sufficiently good are obtained they are generally accepted, and in any case the problem is rarely thrashed out to the bottom, an almost universal defect in commercial research work. Without the help of the National Physical Laboratory the position of the aeroplane in this country would be very different from what it is, and what has been done for the aeroplane requires to be done in many other directions.

But what firm here would do what has been done in the commercial synthesis of indigo, on which it is said that seventeen years' work and over £1,000,000 has been spent by one firm alone abroad? Here in chemical investigations and manufactures the Government refuse to *even* give the help of allowing cheap alcohol to be obtainable, and much of such work is impossible in this country on this account, as in many cases methylated and denatured alcohol are not suitable. Recently under pressure the restrictions have been somewhat relaxed by the Government, but many manufacturers have found that the privileges granted are so tied up in red tape that the concessions are practically useless.

And it is not only on the scientific side that there is so much to be done in the way of putting our house in order; there is much to be done in the way of putting the management and commercial sides of engineering and other allied works in a position to compete.

The great growth of engineering works and their being formed into limited liability companies has not been without its drawbacks.

In the old days an engineering works was comparatively small, and, as a rule, one man, generally a clever engineer, was at the head. After his death, and often before, the place was turned into a limited liability company, and gradually fell into the hands of a body of men, many of them not technical, who had no further interest in the firm than to draw their salaries as directors and managers, and who had no financial stake in the concern beyond the £500 or £1000 in shares necessary to qualify them as directors. The result is that the place gradually degenerates, initiative ceases, and it finally gets to a stage of not paying any dividends, and really being kept going, not for the sake of the shareholders, but of the directors and other officials.

Such a firm as a rule does not put enough aside for depreciation, and thus its machinery and buildings degenerate and become obsolete, which makes it still less able to compete with more modern firms. At the same time it is not able to afford the money necessary to carry on the experimental and research work which is a necessity for any progressive firm, and thus its manufacturers cease to progress with the times. As Sir Charles Parsons truly said, a man or firm in the face of financial difficulties cannot carry on research work, and, further, that the minimum spent on research work should be at least 1 per cent of the turnover, and that the amount it is advisable to spend is 3 per cent. Unless a firm makes good profits it cannot keep up to date, and will sooner or later go to the wall.

But the workman says that he should have his share. What is his share under the present state of things? The average capital expended in an engineering works per individual employed is about £200. An investigation the writer made some years ago gave this figure, and it was confirmed by an investigation of shipbuilding yards, which gave £185, and of the Census of Production, which gives a capital of £1,500,000,000 for 7,000,000 workers, or £214 per man. An investigation of the dividends paid shows them to be about 4 per cent on the capital employed. Here it must be remembered that firms paying 10 to 15 per cent on their ordinary capital have often a large preference and debenture capital, on which a much lower rate of interest is paid, and also that often part of the ordinary capital was issued at a premium. Also account has to be taken of the large number of companies that do not pay any dividend on their ordinary stock, and often none on their preference. Little is as a rule heard of the finances of such companies; it is the ones paying good dividends that public attention is drawn to.

It thus means that the shareholders get about £8 per year per individual employed.

On the other hand, the average wages for men and boys, skilled and unskilled, is about £70 per annum in normal times. This means that the worker gets between eight and nine times as much as the capitalist, and shows on what a very small margin the capitalist works. And without the capitalist, under our present system of individualism, there would be no factories erected and run, and therefore no work for the working-man, a thing it is well for him to remember, and also that without profits the capitalist will not invest in engineering and other works in this country, but will seek for a more profitable field for his capital elsewhere. Every £200 invested in this country in a factory means work and livelihood for one British working-man.

At the same time I am sorry to say the employer does not look after the welfare of his workmen as he might. In a small factory the head of the firm, as a rule, knows all the leading men among the workmen, many of them having been with him for years. As the place grows he loses touch with his men, and as an actual fact knows fewer of those under him when he has 1000 or more employees than he did when he had 400 or under. This state of things gets worse when the place is turned into a limited liability company, as nearly all large places are at present. The result is that a most deplorable state of things has come to pass. The workman says, "Put not thy trust in employers;" the master says, "Put not thy trust in workmen;" and the official who is between the master and the workman says, "Put not thy trust in either."

It is difficult to say what is to be done to remedy this state of things, but one cannot help feeling much might have been done in the past to have prevented such a regrettable state of affairs as there is at present. Much of this trouble might have been avoided if employers had shown more consideration for the welfare of their workmen. Of course, there are some notable exceptions, but they are few and far between. An example is the necessity of the Factory Acts to ensure proper light and air and other arrangements necessary for the health of the workmen. But much more should be done. Why is it that canteens are being rushed up all over the country, and why were there so few before? In many works to this day the provisions for getting food and drink warmed are most primitive and inefficient, and as to getting anything to eat if one has to work overtime unexpectedly, it is in most works impossible. As a rule the only thing available was a drink at the public house outside the gates, and even this is now closed at five o'clock. Why if a man works overtime should he also starve? And how can efficient work be expected under such conditions? Why also should there not be provision for drying clothes after walking to work on a wet morning, and each man be provided with a cupboard where he could keep a change of boots? Why are not sanitary arrangements decently private, and why are they not kept clean and wholesome? they are often in a disgraceful state. These are only a few samples of the directions in which much might be done.

The adjustment of the wages to be paid to the workman is a most difficult one. There are three principal ways of paying workmen: on time, on piece, and on bonus.

On time is the only way of paying a man who is on various classes of work, where the fair time required for each job is not known, and in many cases the most highly skilled men are on such work and as a result only make time wages. This results often in the highly skilled man making less money than the less skilled msn who is on repetition work and as a consequence is working on piece or bonus, and this is obviously unfair. For example, a man may have the setting up and adjusting of a number of machines on repetition work, and he often makes less money than the less skilled men under him who are on piece or bonus, although their nominal rate of wages is less than his.

Again, highly skilled erectors who go outside the works to erect machinery, often worth thousands of pounds, and set it to work, are only paid on time, and often make less money than their fellows who are on piece inside the works.

The adjusting of piece prices is a most difficult one. They should be adjusted so as to be fair both to master and man, but too often such fixing of prices is left to subordinate officials who have in many cases their own axe to grind. There should in every works be a special department for such fixing of prices, and once a price is fixed it should not be altered without good reason. The practice of cutting prices by the masters in the past is, in the opinion of the writer, largely responsible for the present limitation of output by the men, about which we hear so much. There is a rule that if a man makes more than time and half or time and third the price of the job is to be cut. If the price has been fairly fixed why should it be reduced because the man makes large wages due to his skill and industry? The larger the output from his vice or lathe the better for the master, as he is getting a larger output from his plant with a certain capital expenditure, and thereby establishment charges are reduced. This is especially the case in machine work, as the hourly value of the machine employed often far exceeds the wages of the workman employed.

A fair rating for machine tools is 4d. per hour per £100 value, and as the time rating of the man is generally about 9d., it is easily seen that if the average value of the machine tools exceed £225 machine charges exceed time wages, and the average value of machine tools is generally largely in excess of this figure, in fact often about double it. It is therefore obvious that it is much more important to get large output than to pay small wages.

The result of this "time and half" rule is that a good man by working up to the limit of his capacity "spoils the job" for the next man who comes along and may not be of the same calibre as the first man. It has therefore been found advisable and necessary by the workmen to limit the output of all men to a certain standard, and this results in the end by the pace being set by the slowest man on a particular job.

A fair bonus system is perhaps the ideal way of paying men, but here again, although the times for a job are supposed to be fixed and unalterable, in too many cases they have been altered by various devices, and as a result the system is looked on with suspicion by the workman.

Gradually bit by bit the pernicious doctrine that the less work done by a man the more employment there will be has grown up, he not seeing that the cheaper an article can be produced the larger will be the sale for it and the better it will be able to compete with the products not only of other producers in this country but of those abroad. And also that very cheapness, combined with good quality, induces the sale for such articles to be large.

Laziness is inherent in man, and *on an average* no man will work unless compelled to do so, and still less will work his best unless there is a great inducement. This is true not only of the working-man but of all other classes. Therefore the policy of "ca' canny" has been only too readily adopted, on the ground not only that it was pleasant for the man himself but also he believed that it tended to the welfare of his fellow-workmen.

The writer has very reluctantly come to the conclusion that the workman of to-day is not doing as much work as was done some thirty years when he was in the shops, and not only this, but that timekeeping is not as good. In this connection, however, it must be remembered that excessive overtime inevitably leads to bad timekeeping.

Bad timekeeping causes much more loss than that due to the actual time lost, as not only does machinery and other plant lie idle, but the disorganisation caused in a works by lost time is most serious.

With the growth in strength of the Trades Unions, which at first were for the legitimate object of seeing that the workman got fair play, and providing out-of-work and old-age benefits, &c., has grown up a system of Trades Union officials who live by agitation, and whose job would be gone if there were no supposed grievances to agitate about. These men keep the labour world in a constant state of agitation, and make the employers' and officials' existence a burden to them by constant demands of all sorts, many of them utterly impracticable and unfair. When they cannot agitate against the employer they agitate against another Trades Union, and thus endless disputes spring up on the demarcation of work. Some of the worst strikes in the past have been due to disputes between two Trades Unions.

Unless something can be done to bring master and man together and make both work for the common good, English trade must inevitably go down, and the supremacy that England has in the engineering of the world will come to an end.

Nothing ever was a truer statement than that recently made by Lord Joicey that this country, unless it produces as cheap or cheaper than other countries, cannot in the long run keep her trade, and this is true in spite of any tariff walls which may be set up. And if the present state of affairs is maintained of unscientific management and obsolete machinery, combined with limitation of output and high wages, or, in other words, high cost of production, we must, sooner or later, go to the wall.

What is really wanted is common honesty and common sense on both sides, for one side is as bad as the other at present.

And now about the official, who is in all grades from the manager down to the foreman, and who comes between the master and the man. Unless he is treated fairly by the master, and unless he treats his men fairly, there is sure to be friction and loss of efficiency. He must also work with his fellow-officials, who move in lines more or less parallel to his, and here, to prevent jealousies and to prevent the more unscrupulous among them taking unfair advantages, demarcation of each official's duties and work is most important. This is a point often omitted to be taken sufficiently into account in the organisation of a works, and often causes most disastrous results. The duties of each man should be clearly defined by the master, and no interference with those of others tolerated. The master also should remember that the official has no Trades Union or similar organisation to protect him, and should act accordingly. Much more could be said about the relations of the official both with his fellow-official who is on the same level as himself, with his master who is above him, and the workman who is under him, but time forbids. On all three sides much improvement could be effected. The fact remains, however, that for success it is essential that all, from the apprentice to the head of the firm, should work as one homogeneous whole.

Apart from the considerations set out above, combinations among the firms employed in any one trade are most essential for the wellbeing of that trade. It is by such combination that much of the progress made of late years by our competitors has been effected. Some of these combinations have been international, and at least two such in the engineering trade before the war were so. These now, of course, are, and it is expected will be after the war, confined to the allied and possibly to neutral countries, but such combinations, whether among all the engineering firms in one district or among firms employed in one particular trade, to be successful must be worked fairly to all members, and the larger firms must not override the smaller, as, it is regrettable to say, has been done in combinations of employers in some districts. For example, in a district where there is one firm very much larger than any of the others, it is not unknown for it to act the bully and insist on everything being done as would suit its requirements, regardless of the rights of others. And, further, such combinations are, unless directed by men with broad minds and able to take a wide view of things, liable, especially in case of emergency, to do much harm.

If the Armament Ring in this country had taken such a view when it was found what an enormous supply of munitions was required, it is doubtful if there would have been such a shortage as there has been. Hundreds of firms were willing and anxious to help in the production of munitions, but when they offered their services they were met in many cases with a blank refusal, and in all cases with little encouragement. And when, under pressure from the Government, the Ring accepted outside help, in many cases the conditions imposed on the subcontractors were unfair in the extreme, apparently the whole idea of the Ring being to make all the profit they could out of the troubles of the Empire. It has been just as difficult to persuade the Armament Ring to give up what they thought was their monopoly and to bring in outside works to help in the production of munitions as it has been to persuade the Trades Unions to forego trade customs and to enable outside sources of labour to be employed, such as women and other unskilled labour. But both have had to do it. In other words, "Dilution of Works" has been as difficult to effect as "Dilution of Labour," and the position of both the Armament Ring and of the workman would have been very different if they had consented freely to it when it became obviously necessary for the safety of the Empire.

Combination among workmen is admittedly a necessity if they are to have fair play, but combination among employers has come later and is equally a necessity.

At present most of the principal federations of employers deal only with wages questions and questions affecting labour, but they require to be extended so as to take in all branches of the business of engineering. Labour has long seen the importance of federation, it is now for Capital to do the same. One of the great difficulties has been that certain firms would not join, and a very small proportion acting thus weakens the whole to a much greater extent than the actual ratio of this small proportion of the whole. It is easy to see how alive Labour is to this by the constant trouble over the Non-Union question, and this is well put in the notice addressed last March to the Transport Workers of the Mersey district: "To be outside a Union is to be disloyal not only to your own class but to yourselves individually." What applies to Labour also applies to firms, for a firm to be outside the Federation is to be disloyal, not only to its fellow-firms but to itself.

Such a state of affairs is not tolerated in some of the countries competing with us, and it is questionable whether action by the Government is not advisable.

An example of the mischief done by a few who would not fall into line with the many is seen by the necessity for the Act compelling the early closing of shops one day a week. The great majority were ready to close, but the action of a small minority prevented their doing so, and in the end compulsion had to be used on the minority. Legislation has not been necessary to prevent "blacklegging" in the labour world since other methods have been used which have been practically successful. but it is quite possible it may be necessary to use compulsion to make firms toe the line.

Such combinations are not only for labour questions but also for all other subjects affecting the engineering industry at large, and more especially the special industries in which any one firm deals. Thus they resolve themselves into general federations of all engineering industries and minor ones dealing with particular trades.

The former deal chiefly with labour questions and questions affecting the industry as a whole, the latter with those affecting any particular trade.

Among the questions coming up to be considered by the latter class is the standardisation of specifications and conditions of contracts as well as in some cases the adjusting of prices to avoid unfair competition and to put the whole trade on a paying basis. Much has been done in this direction with most advantageous results in certain cases, but much more remains to be done if this country is going to hold its place in the world.

The necessities of research work have already been dealt with, and by the pooling of such research work enormous advantages in any one trade could be obtained. Such pooling of information has been effected with most beneficial results, especially in the chemical trade abroad. Any workable scheme which would enable this to be done and get over the jealousies between one firm and another would be of enormous benefit to the trade in general.

Another thing that must not be lost sight of is the urgent need of improving our educational system. It is little short of a disgrace that the older universities are closed to those without a knowledge of Latin and Greek.

Languages are of the greatest importance to an engineer, but not dead languages but live ones. And these should be properly taught, so that the student should not only be able to read and write them but also to speak and understand them. It is quite a different knowledge of a language to be able to read, write, speak, or understand it. Many people can read a language without being able to write, speak, or understand it, and conversely it is not uncommon to meet people who can speak and understand a language without being able to any large extent to read or write it. And it is only in live languages that a man is trained to speak and understand a language.

Why is it that we are so wedded to the dead languages? There is, of course, the tradition that such are necessary for a liberal education, and there is the argument that modern languages are not as good a training for the mind. Granted that they are not quite so good from the point of view of learning to read and write them, does not the fact that they can also be taught as a live language to be spoken and understood make them on the whole the best educationally for a man? This is entirely apart from the fact that modern languages are useful and ancient useless to the man in commercial work. There is, of course, bitter opposition from that most conservative man, the schoolmaster, and one great reason is that it is much easier and cheaper to get a man to teach Latin and Greek than modern languages which have to be taught orally. The teaching of Latin and Greek as it is usually taught has been standardised to the last degree, and as a result they can be taught by the "semi skilled" man, and a "skilled" man is not necessary, to use engineers' phraseology. In fact teaching of Latin and Greek is a pure "repetition job." At the same time no education is complete unless science is combined with languages and also literature, and here lies one great danger of modern technical education.

And after the boy has left school and enters the shops more facilities should be given to enable him to not only keep up but continue his education. In the shops and drawing office too often the boy is left to pick up a knowledge of his trade as best he can. The apprentice who asks questions is often looked on as a nuisance, and requests for information are generally met by a blank refusal or worse. Often the foreman or chief draughtsman is afraid to answer questions for fear of being charged with giving away so-called "trade secrets," but an immense deal of information can be given to an apprentice without doing so.

Evening classes are all very good in their way, but more facilities should be given for the diligent apprentice to attend day classes, and this can be arranged in various ways if the employer has a will to do it. A thing that at present often prevents boys desirous of educating themselves getting on is the fact that overtime is allowed as soon as a boy is eighteen, and often he is compelled to work overtime regardless of classes that he ought to be attending.

It is important to remember that the boy of to-day is the man of to-morrow.

One complaint is that after a lot of trouble is taken about a boy he leaves after a few years and goes to another employer. The good of the trade in general must be considered, and a man who has had experience of various classes of work is generally a much more valuable man than one whose knowledge is confined to one class only. In any case the other employer gets the benefit of what has been done by the first, and thus the trade in general benefits.

It is felt that this is a very imperfect review of things as they are at present, but if this address induces all classes engaged in engineering to consider how things can be bettered the author feels that a part, at all events, of his object has been attained.

THE BRITISH ASSOCIATION ON THEIR VISIT TO SEE A PORTABLE WOOD DISTILLATION PLANT AT THE CROWN WOODS OF CHOPWELL, COUNTY DURHAM.

PROF. CROWTHER, the Recorder of Section M, and Principal Foulkes, the Secretary of the Agricultural Education Association, with about thirty other members, were conducted to Chopwell Woods by Mr. S. H. Collins, Adviser in Agricultural Chemistry, and Mr. J. F. Annand, Adviser in Forestry, and Manager of the Woods.

Prior to the inspection of the Portable Distillation Plant, Mr. Annand conducted the party over a part of the Woods. He explained the system of management which has been in operation since the Woods were taken over by Armstrong College. Chopwell Woods have been Crown property since the time of Queen Elizabeth, and at one time were managed for the growth of oak for the navy. Oak forest does not now pay as formerly on poor land, and large portions of the poor quality oak woods and coppices at Chopwell are now being converted into conifer forests. Crooked and rough oak tops, &c., are of no value to the timber merchant, as they are not even suitable for pit props. This remark also applies to the hardwood stumps left in the ground after felling, which are found injurious, inasmuch as they constitute breeding ground for various fungoid diseases which attack succeeding timber crops. Some means of disposing of, and utilising, this waste has therefore to be devised before the new crops can be laid down. One method is wood distillation. The object of the experimental distillation plant at Chopwell, Mr. Annand pointed out, was therefore to utilise and dispose of the branch wood and other waste, and to obtain saleable products from them. These products consist of:—

(*a*) Wood charcoal of high quality.
(*b*) Wood tar.
(*c*) Crude acetic acid.
(*d*) Gases.

On arrival at the plant, Mr. Collins explained that the plant is a portable one, but is only moved at long intervals. The chief part is a horizontal retort mounted on wheels and surrounded by a jacket which forms the flue of the fire used for heating. The solid product is charcoal, and remains in the retort. The liquid products are tar and crude pyroligneous acid, and after passing through condensing pipes leading from the retort, these are collected in barrels. The gaseous products are used for fuel. The tar has been sold for ship-building purposes, but a much better use is to assist in making up wood preservatives for fences, rails, and building material for use on estates.

The pyroligneous acid is treated with lime, and, after settling, boiled down in a pan over the fire used for heating the retort. The resulting product is acetate of lime. About one ton of wood fills the retort, from which 5 cwt. charcoal of the highest class is obtained. This charcoal finds a ready market.

So far the trouble has been the lack of labour, but in spite of difficulties the current income has exceeded the current expenditure about 5 per cent, and stores of products have been collected for future sale against depreciation of plant.

THE RARE EARTHS.

By Prof. ALEX. FINDLAY, M.A., F.C.S.

THE great national stocktaking that has lately been going on has revealed some startling facts as to the extent to which we have been allowing some of the most important natural resources of our Empire to pass out of our control. Mineral and vegetable wealth was there, but in two many cases the wealth came not to us but to those with whom we are now in armed conflict; and not the least important problem to which this war has opened our eyes is the more thorough and effective utilisation of these natural resources for the benefit of our own peoples and for the furtherance of imperial unity, industry, and commerce. Gradually German control over the raw materials of industry contained within the British Empire is being broken down, and one of the most recent steps in this direction has been the loosening of the enemy's grip on the Indian deposits of monazite sand, the chief raw material on which the rare earth industries depend.

The story of the discovery and utilisation of the rare earths goes back to 1788, when in a quarry on the Island of Ytterby, near Stockholm, there was found a mineral from which, a few years later, a Finnish chemist, Johann Gadolin, isolated a new metallic oxide or "earth" (to use an older terminology), now known as yttria. It was the first of a series of about sixteen new "earths" which the investigations of succeeding years, down to the present day, have given to chemical science. Although widely distributed throughout the world, from the Ural Mountains to the Carolinas, and from Brazil to India and Japan, these rare earths, as the term implies, occur in no great abundance; and even their names, or the names of the elements from which they are derived—for example, yttrium, scandium, cerium, praseodymium, samarium, europium, terbium, lutecium, and we may add—although they are no longer rare, thorium and zirconium—are for the most part unknown except to the student of chemistry.

The rare-earth elements, on account of their very closely related properties—so closely related that it is only by the most refined methods of investigation that the differences can, in some cases, be detected—have offered to chemists for many years some of the most puzzling ot problems, and have even caused doubt to arise concerning the precise interpretation to be placed on some of the most fundamental concepts of chemical science; and their fuller investigation may, in due time, be destined to transform the whole science of chemistry. Sir William Crookes, the foremost British investigator of the rare-earth elements, has, indeed, stated his belief that "by following the study of them to the utmost limits, we may arrive at the explanation of what chemical elements really are and how they originated, and discover the reasons for their properties and mutual relations. When this knowledge has been wrested from Nature, chemistry will be established upon an entirely new basis. We shall be set free from the need for experiment, knowing *à priori* what the result of each and every experiment must be; and our knowledge then will as much transcend our present scientific systems as the knowledge of the skilled mathematician of the present day exceeds that of primitive man, counting on his fingers."

But if the rare earths are destined to furnish us with the key of one of Nature's most profound secrets, they have also shown themselves, in some cases, to possess great practical value in the everyday life of man. Although it was in 1794 that the first of the rare earths was discovered, it was not till 1883 that they began to find any useful application. About that time Carl Auer von Welsbach was engaged on a purely scientific investigation of the rare earths in the laboratory of Bunsen at Heidelberg, and in the course of his investigation he was struck by rhe fact that some of these oxides (earths) emitted a light of dazzling brilliance when strongly heated. In that observation, made in the course of an investigation which had, apparently, no practical importance, the enormous industry of the incandescent mantle manufacture was born. As material for the "mantle," various rare earths ana mixtures were tried, but practical success was not attaine till 1891, when von Welsbach made the interesting discovery that although neither thoria (oxide of thorium alone, nor ceria (oxide of cerium) alone, possessed much light-giving power, a mixture of 99 per cent of thoria with 1 per cent of ceria emitted a brilliant light; and increase or diminution in the amount of ceria was accompanied by a decrease in the light-giving power of the mixture. Foi the production of the mantles tubes woven of ramie fibre or of artificial silk—the production of which from wood-pulp constitutes one of the most notable of the recent achievements of applied chemistry—are impregnated with a solution containing the nitrates of thorium and cerium in the proper proportions; and when these tubes are dried and incinerated the woven fabric is burned away and the nitrates are converted into a mixture of the oxides of thorium and cerium, which form a mesh-work in imitation of the structure of the woven material. By the discovery of the incandescent mantle, the doom of the gas-lighting industry was stayed; and the importance of the new industry can be gauged by the fact that upwards of three hundred million mantles are now manufactured annually.

The invention of the Welsbach incandescent mantle created at once an enormously increased demand for thoria, which till then had been extracted, for the most part, from a mineral thorite, a silicate of thorium, found mainly in Scandinavia. The greatly enhanced price of the mineral stimulated an active search for other sources of supply, and these were soon found, more especially in the heavy, golden-yellow monazite sands occurring in various parts of the world. Monazite consists mainly of the phosphates of the rare-earth metals (cerium, lanthanum, &c.), along with 5 or 6 per cent of thoria, and constitutes the main source of the world's supply of thorium and of the rare earths. The first deposits to be worked were in the Carolinas, and until 1895 these deposits, worked mainly by an American company, supplied the world's demand for thorium. In that year, however, the German Thorium Syndicate, having acquired the right of working the much more advantageously situated deposits along the shores of the southern provinces of Brazil, entered into competition with the American Company, and, after a struggle lasting about fifteen years, forced the latter to cease work. Mistress now of the situation, Germany determined to remain so, and when deposits of monazite sand were discovered in Travancore, India, in 1911—deposits even more valuable and rich in thoria than those of Brazil—the Auer Company of Berlin succeeded in obtaining virtual control of the company formed to work the deposits. The whole output went to German firms, who derived an enormous profit from the sales of a small portion of the sand and thorium products to British manufacturers. But war has now broken that monopoly and has given to British manufacturers the free utilisation of one of the valuable natural resources of the Empire.

Besides its use in the incandescent mantle, there is another direction in which thorium promises to be of benefit to man, owing to its possessing the remarkable property of radio-activity, first discovered by the eminent French physicist, Henri Becquerel, in 1896. In the process of atomic degradation, thorium gives rise to meso-thorium, a substance three hundred times more active even than radium: and as meso-thorium can be readily separated, together with the small amount of radium also present, in the process of isolating the rare earths from monazite sand, it promises to come into increasing use for surgical and other purposes in place of the much more expensive radium.

The incandescent mantle, we have seen, does not consist entirely of thoria, but contains also a small amount of ceria, an earth which is also obtained from monazite. Whereas, however, the incandescent mantle contains only 1 per cent of ceria and 99 per cent of thoria, monazite contains only from 5 to 10 per cent of thoria and 50 to 60 per cent of ceria and other rare earths. In the course of time, therefore, large quantities of these rare earths accumulated, awaiting the discovery of some use to which they might be put. This discovery was made in the early years of the present century, also by Auer von Welsbach, who found that when an alloy of iron and the cerium metals was rubbed or scratched with a piece of hard steel, an abundance of bright sparks was given off; and the mechanical fire-producers in which the sparks struck from this and other alloys of the rare-earth metals are caused to ignite tinder or the vapour of some inflammable liquid, are now almost as familiar as the ordinary match. Compounds of cerium have also found application in medicine, as catalysts in the production of the dye, aniline black, and as "reducing" agents in photography. For others of the rare earths, yttria, thoria, and zirconia, use was formerly found in the manufacture of the rods used in the Nernst lamp, now almost entirely superseded; and zirconia (found occurring naturally) is largely used in the production of the Drummond or "lime" light, and for the manufacture of crucibles which not only withstand a very high temperature, but can be plunged white-hot into cold water without breaking.

If investigations of, apparently, purely scientific interest formed the basis on which the industrial utilisation of the rare earths has been built, pure science has, in its turn, reaped great advantage from the extent to which these later industrial developments have placed large quantities of the rare earths at the disposal of the scientific investigator; and time may show that this is not the least of the benefits which the industry of the rare earths has conferred on mankind.—*New Statesmen*, September 16, 1916.

HALOGENATION.
CHLORIC ACID AS A REAGENT IN ORGANIC CHEMISTRY.

By RASIK LAL DATTA
and
JOGENDRA KUMAR CHOUDHURY.

THE preparation of organic chlorates has not been attempted with the exception of a few isolated instances. It was thought desirable to study the chlorates of organic bases systematically, as also the action of chloric acid on organic compounds in general.

Chlorates have been prepared either by the direct action of chloric acid on the organic base, or by means of double decomposition between the hydrochloride of the base and silver chlorate. They form readily with the aliphatic bases according to either of the above methods, but in the case of aromatic bases the action is quite different. Sometimes the chlorate could not be formed at all since the base undergoes oxidation rapidly. With an excess of chloric acid the decomposing bases form brown to yellow oily substances which consist, generally, of the lower chloroquinones. With regulated amount of chloric acid the decomposing substances form dyes. It has also been found that iodo derivatives of aromatic hydrocarbons readily form iodoxy compounds when subjected to its prolonged action.

Chlorates are, as a rule, either explosives or highly unstable in the dry state, and special precautions must therefore be taken to determine their melting or decomposition point. Not all explode, however, some melting quite harmlessly and some with more or less decomposition. When held in a flame or touched with a drop of concentrated sulphuric acid these chlorates burn off suddenly, in some cases with production of a sharp report. Chlorates of aromatic bases sometimes go off spontaneously, specially if the chlorate has been obtained by the direct action of chloric acid on the base, probably as the result of a little free chloric acid which might be present. Such spontaneous explosion does not take place if the chlorate be purified by recrystallisation from alcohol.

The analysis of these chlorates is carried out by mixing with a large quantity of powdered copper oxide.

Experimental.

Action of Chloric Acid on Aniline.—Aniline chlorate has been prepared before by direct neutralisation (Beamer and Clarke, *Ber.*, 1879, xii., 1066; L'Hate Gerard, *Ann.*, [6], xxii., 404). It has been found that when aniline is mixed with quite an excess of chloric acid a vigorous reaction, with the evolution of a considerable amount of heat, takes place, and as a result of the action a brown oil is formed which settles at the bottom. The oil consists of a mixture of the lower chloroquinones which is under examination. But if a little chloric acid is added to an excess of aniline and the mixture allowed to stand at the ordinary temperature it undergoes gradual oxidation, and finally a black substance is precipitated. This has been found on examination to be aniline black, giving all its reactions. (Found, N = 15·48; calc., N = 15·34). The yield obtained is quantitative.

o-*Toluidine Chlorate*, $C_7H_9N.HClO_3$.—To an excess of *o*-toluidine, chloric acid is added drop by drop, when crystals begin to make their appearance. Care is taken not to add an excess of chloric acid, as the presence of a little free acid will decompose the substance explosively at ordinary temperature, a slight excess of toluidine being maintained. The crystals are filtered with suction, washed thoroughly with ether and benzene, and finally recrystallised from alcohol when it is obtained in white plates.

0·1642 grm. gave 0·2652 grm. CO_2 and 0·0735 grm. H_2O; 0·0594 grm. gave 4·1 cc. N_2 at 28° and 763 mm.; 0·1435 grm. gave 0·1068 grm. AgCl.
Calc. for $C_7H_9N.HClO_3$—C, 43·86; H, 5·22; Cl, 18·5. Found—C, 43·77; H, 5·25; N, 7·6; C, 18·63 per cent.

The crystals are not indefinitely stable in air, but turn grey, and finally produce a black substance which, as will be shown later, is also formed by the prolonged action of chloric acid on *o*-toluidine. *o*-Toluidine chlorate explodes at 88°. When a flame is applied to it, it burns explosively.

It has also been found that on adding an excess of chloric acid to a little *o*-toluidine a blue coloured solution is produced, and the mixture becomes hot. This is followed by a vigorous reaction with boiling, and a brown-black viscous liquid separates at the bottom. This substance is under examination.

If an excess of *o*-toluidine is left in contact with chloric acid and the vessel cooled with water so as to avoid any vigorous reaction, the toluidine is slowly transformed into a black insoluble substance which gives some of the tests of *o*-toluidine black. The dye has been found to be quite distinct from *o*-toluidine black, and is under systematic examination. The same dye is obtained by the gradual decomposition in air of *o*-toluidine chlorate, as has been already noticed.

p-*Toluidine Chlorate*, $C_7H_9N.HClO_3$.—For the preparation of this compound *p*-toluidine is dissolved in ether, and to it an aqueous solution of chloric acid is added drop by drop, taking care to keep the *p*-toluidine in slight excess. The ether is then allowed to evaporate at the ordinary temperature as rapidly as possible. As the ether evaporates long white crystals remain behind. The crystals are washed with ether and benzene, and finally recrystallised from alcohol.

0·2110 grm. gave 0·3405 grm. CO_2 and 0·0993 grm. H_2O; 0·0594 grm. gave 3·85 cc. N_2 at 26° and 764 mm.; 0·1552 grm. gave 0·1157 grm. AgCl.
Calc. for $C_7H_9N.HClO_3$—C, 43·86; H, 5·22; N, 7·32; Cl, 18·54. Found—C, 43·22; H, 5·33; N, 7·33; Cl, 18·78.

p-Toluidine chlorate explodes at 125°, giving off a large amount of white fumes, and takes fire suddenly when a flame is applied to it. The substance on exposure to air gradually turns grey owing to slow decomposition of the salt.

Similarly to *o*-toluidine, it has been found that on treating *p*-toluidine with an excess of concentrated chloric acid a vigorous reaction begins in the course of half-an-hour with considerable evolution of heat, and as a result of the reaction a brown viscous oil, which is under examination, settles at the bottom. But if an excess of *p*-toluidine be kept with a little dilute solution of chloric acid in the cold the mixture gradually turns black, and the *p*-toluidine is ultimately converted into a black dye. The dye is under examination.

p-*Phenylenediamine Chlorate.*—Chloric acid, when added directly to *p*-phenylenediamine, dissolves it, and gives a deep blue solution which gradually assumes a brown colour. If an ethereal solution of the diamine is mixed with chloric acid on a watch-glass and the ether is allowed to evaporate rapidly, crystals are obtained. They could hardly be separated for purification as the material soon turns black. The same black dye is obtained when *p*-phenylenediamine is left in contact with chloric acid in the cold. The systematic investigation of the dye is in progress.

An attempt was made to obtain *m*-phenylenediamine chlorate by double decomposition between *m* phenylenediamine hydrochloride and silver chlorate. The resulting solution began to turn dark as soon as double decomposition was complete. On allowing the solution to evaporate in a vacuum instead of the chlorate, a grey-black dye is left behind. The further examination of this black substance is in progress.

Benzylamine Chlorate, $C_7H_9N.HClO_3$.—For the preparation of the chlorate an excess of benzylamine is mixed with an aqueous solution of chloric acid. The resulting solution is allowed to evaporate on the water-bath, and the product remains melted over it. On cooling, the liquid solidified in nice crystalline plates which are slightly yellow in colour owing to the presence of benzylamine. To free it from benzylamine it is washed thoroughly with ether, and finally purified by recrystallisation from alcohol.

0·1825 grm. gave 0·2934 grm. CO_2 and 0·0856 grm. H_2O; 0·0730 grm. gave 4·75 cc. N_2 at 23° and 765 mm.

Calc. for $C_7H_9N.HClO_3$—C, 43·86; H, 5·22; N, 7·32. Found—C, 43·83; H, 5·62; N, 7·6 per cent.

Benzylamine chlorate melts at 110·5° to a yellow liquid. It is hygroscopic, and dissolves in water and alcohol, but not in ether and benzene.

Benzylmethylamine Chlorate, $C_6H_5CH_2NHCH_3.HClO_3$.—Equivalent quantities of benzylmethylamine and chloric acid are mixed with a slight excess of the former. The mixture is first heated on the water-bath for about an hour, and is then allowed to cool in a desiccator. The solid mass thus obtained is then washed thoroughly with ether, and recrystallised from alcohol and dried.

0·1405 grm. gave 0·2352 grm. CO_2 and 0·0674 grm. H_2O; 0·1038 grm. gave 6·3 cc. N_2 at 23° and 762 mm.

Calc. for $C_8H_{11}N.HClO_3$—C, 46·7; H, 5·84; N, 6·81. Found—C, 45·52; H, 5·99; N, 7·02 per cent.

The chlorate melts at 59·60°. It is soluble in water and alcohol, but not in ether and benzene. It burns off suddenly when a flame is brought near to it.

Benzylethylamine Chlorate, $C_6H_5CH_2.NHC_2H_5.HClO_3$.—Equivalent amounts of benzylethylamine and chloric acid are mixed and heated on the water-bath for some time. On cooling, crystals separate which are thoroughly washed with ether and recrystallised from dilute alcohol.

0·1010 grm. gave 0·3626 grm. CO_2 and 0·1052 grm. H_2O; 0·1588 grm. gave 8·85 cc. N_2 at 24° and 763 mm.

Calc. for $C_9H_{11}N.HClO_3$—C, 49·2; H, 6·38; N, 6·38. Found—C, 49·19; H, 6·55; N, 6·33.

The chlorate melts at 81·5°. It takes fire suddenly when a flame is applied to it. It is very soluble in water and alcohol, but insoluble in ether and benzene.

Piperazine Chlorate, $C_4H_{10}N_2.2HClO_3$. — Piperazine chlorate is prepared by double decomposition between silver chlorate and piperazine hydrochloride. On evaporation of the solution in a vacuum over sulphuric acid the chlorate is obtained in nice white shining crystalline plates. On presenting a flame to it, it takes fire suddenly. It decomposes between 98 and 100°. In this case the decomposition was not explosive.

0·2215 grm. gave 22·2 cc. N_2 at 24° and 760 mm.; 0·1234 grm. gave 0·1378 grm. AgCl.

Calc. for $C_4H_{10}N_2.2HClO_3$—N, 10·98; Cl, 27·8. Found—N, 11·22; Cl, 27·91.

Ethylenediamine Chlorate, $C_2H_4(NH_2)_2.2HClO_3$.—This chlorate is prepared by neutralising ethylenediamine solution with chloric acid by the help of a litmus paper, and evaporating the resulting solution on the water-bath to crystallisation where the substance is obtained in shining white flat crystals. As thus obtained it is quite pure, and a single recrystallisation from water or alcohol gives a very pure product. It decomposes at 150°. Like the other chlorates it burns off with a flash on presenting a flame to it.

0·1825 grm. gave 19·85 cc. N_2 at 25° and 760 mm.; N, 12·23

Calc. for $C_2H_4(NH_2)_2.2HClO_3$—N, 12·23.

Guanidine Chlorate, $CN_3H_5.HClO_3$.—This is obtained by the double decomposition between guanidine sulphate and barium chlorate, and evaporating the resulting solution over a water-bath, when white crystals are obtained. It decomposes at 148°, and does not explode sharply at that temperature. However, it burns away on presenting a flame to it, or touching with a drop of concentrated sulphuric acid.

0·1010 grm. gave 26·3 cc. N_2 at 23° and 767 mm.

Calc. for $CN_3H_5.HClO_3$—N, 29·8. Found—30·62.

Menthylamine Chlorate, $C_{10}H_{19}NH_2.HClO_3$.—This has been prepared by the double decomposition between menthylamine hydrochloride and silver chlorate, and evaporating the solution in a vacuum over sulphuric acid. The chlorate is then left in beautiful white crystalline needles. It melts at 168°. This chlorate, unlike the previous one, does not flash off when a burning stick is brought near it, but it simply melts.

0·0828 grm. gave 4·4 cc. N_2 at 24° and 762 mm.; N, 6·07.

Calc. for $C_{10}H_{19}NH_2.HClO_3$—N, 5·85.

Pyridine Chlorate, $C_5H_5N.HClO_3$.—When a slight excess of pyridine is mixed with concentrated chloric acid and the mixture is heated on the water-bath, crystals of the chlorate are left. They are washed with water, and recrystallised from alcohol, and then melt with decomposition at 147°.

0·1021 grm. gave 7 6 cc. N_2 at 23° and 766 mm.; 0·1827 grm. gave 0·1592 grm. AgCl.

Calc. for $C_5H_5N.HClO_3$—N, 8·56; Cl, 21·7. Found—N, 8·58; Cl, 21·92.

Pyridine chlorate burns with a sudden flash. It also takes fire when concentrated sulphuric acid is allowed to come in contact with it. It is soluble in water and alcohol, but does not dissolve in non-dissociating organic solvents. The crystals are soft and soapy to the touch, and give the odour of pyridine.

Quinoline Chlorate, $C_9H_7N.HClO_3$.—This has been prepared by mixing chloric acid with rather more than the theoretical amount of quinoline, and evaporating on the water-bath. The crystals obtained are washed with a mixture of alcohol and ether for purification. The compound melts at 66–67°.

0·1117 grm. gave 6·65 cc. N_2 at 25° and 760 mm.

Calc. for $C_9H_7N.HClO_3$—N, 6·56. Found—N, 6·76.

The chlorate has a slightly yellowish tinge, and is very hygroscopic. It is soluble in alcohol and water, but cannot be successfully recrystallised from these solvents as the substance obtained on evaporating the solvents sets to a hard mass on drying. It decomposes with a flash, and a large amount of smoke when a flame is applied to it, or when touched with concentrated sulphuric acid, leaving a black residue behind.

Tetramethylammonium Chlorate, $N(CH_3)_4ClO_3$.—This is prepared by the double decomposition between tetramethylammonium iodide and silver chlorate, and evaporating the resulting solution on the water-bath to crystallisation. As thus obtained it consists of white crystals. It is freely soluble in alcohol and water. It explodes at 230°. It takes fire suddenly on presenting to a flame or touching with a drop of concentrated sulphuric acid.

0·0659 grm. gave 5·25 cc. N_2 at 3° and 765 mm.; N, 9·02.

Calc. for $N(CH_3)_4ClO_3$—N, 8·89.

Tetraethylammonium Chlorate, $N(C_2H_5)_4ClO_3$. — This has been similarly prepared by the double decomposition between tetramethylammonium iodide and silver chlorate, and evaporating the resulting solution on the water-bath to crystallisation when crystals are obtained on cooling. As thus obtained the substance is quite pure. It can be recrystallised from water or alcohol. It melts with decomposition at 223°. It takes fire as usual when a flame is applied to it or when it is touched with a drop of concentrated sulphuric acid.

0·0895 grm. gave 5 cc. N_2 at 24° and 766 mm.; N, 6·4.
Calc. for $N(C_2H_5)_4ClO_3$—N, 6·56.

Tetrapropylammonium Chlorate, $N(C_3H_5)_4ClO_3$.—This has been obtained as usual by the double decomposition between silver chlorate and tetrapropylammonium iodide, and evaporating the resulting solution on the water-bath to crystallisation. The chlorate melts at 217° without decomposition. It dissolves freely in water and alcohol. It burns off as usual on the presentation of a flame or when touched with concentrated sulphuric acid.

0·1444 grm. gave 3·9 cc. N_2 at 25° and 767 mm.; N, 5·52.
Calc. for $N(C_3H_5)_4ClO_3$—N, 5·2.

Dimethylphenylbenzylammonium Chlorate,—

$$N(CH_3)_2(C_6H_5)C_7H_7ClO_3.$$

—This salt is prepared from dimethylphenylbenzylammonium bromide and silver chlorate by double decomposition, and evaporating the solution in a vacuum over sulphuric acid. The chlorate obtained is white and crystalline in shape. It is hygroscopic, and dissolves freely in water and alcohol. It decomposes without any sharp explosion at 137°, leaving a red mass as residue which does not melt on further heating. It, however, burns with a flash, and decomposes explosively with concentrated sulphuric acid, and slowly decomposes to a grey mass on leaving it at the ordinary temperature for several days.

0·1527 grm. gave 6·75 cc. N_2 at 24° and 763 mm.; N, 5·0.
Calc. for $N(CH_3)_2(C_6H_5)(C_7H_7)ClO_3$—N, 4·74.

Diethylphenylbenzylammonium Chlorate,—

$$N(C_2H_5)_2C_6H_5C_7H_7ClO_3.$$

—This is prepared as usual by the double decomposition between the corresponding chloride and silver chlorate, and evaporating the resulting solution in a vacuum over sulphuric acid. This is obtained in white crystals melting to a dark liquid at 77°. On further heating it becomes darker and darker until at 125° it decomposes with effervesence. It decomposes partly on leaving it for long periods in the air. It is soluble in water and alcohol, and burns with a flash.

0·1623 grm. gave 6·1 cc. N_2 at 765 mm.; N, 4·24.
Calc. for $N(C_2H_5)_2C_6H_5C_7H_7ClO_3$—N, 4·33.

Trimethylsulphine Chlorate, $S(CH_3)_3ClO_3$.—This salt is obtained by the double decomposition between silver chlorate and trimethylsulphine iodide, and evaporating the resulting solution on the water-bath. The salt could be recrystallised from water with difficulty since this salt is very soluble in cold water, and the difference in solubility in hot and cold water is very small. It explodes at 170°. The salt explodes sharply on presenting a flame to it, the explosion being very rapid and sharp. It is hygroscopic, and liquefies when exposed to air.

0·1474 grm. gave 0·1212 CO_2 and 0·0666 grm. H_2O; C, 22·32; H, 5·91.
Calc. for $S(CH_3)_3ClO_3$—C, 22·44; H, 5·61.

Oxidation of Organic Iodo-compounds by means of Chloric Acid.

Iodoxy-benzene, $C_6H_5IO_2$.—A little iodobenzene is taken in a crystallising dish, and to it is added an excess of concentrated chloric acid solution and kept aside for about two days. In the course of this period slightly yellow crystals appear. On washing with alcohol, in which it is insoluble, it is obtained in clear white crystals. The substance explodes at 227—228°. An iodine estimation gave the following results:—

0·1251 grm. gave 0·1251 AgI; I, 54·03.
Calc. for $C_6H_5IO_2$—I, 53·81.

o-*Iodoxy-toluene*, $CH_3.C_6H_4IO_2$.—This is obtained similarly to the above substance by allowing *o*-iodotoluene to remain in contact with chloric acid for several days. A crystalline product is obtained which is thoroughly washed with alcohol and separated by filtration. The product decomposes at 210°.

0·0855 grm. gave 0·0854 AgI; I, 51·04.
Calc. for $CH_3.C_6H_4IO_2$—I, 50·8.

p-*Iodoxy-toluene*, $CH_3.C_6H_4IO_2$.—This is obtained by exactly the same procedure as the previous compound. *p*-Iodotoluene is left for several days in contact with chloric acid. The crude product thus obtained is washed with alcohol. It decomposes at 229°.

0·1213 grm. gave 0·1133 AgI; I, 50·73.
Calc. for $CH_3.C_6H_4IO_2$—I, 50·8

Iodoxy-m-*xylene*, $C_6H_3(CH_3)_2{}^{1\cdot3}(IO_2)^4$.—This is obtained by keeping the iodo-compound with a strong solution of chloric acid for two or three days at ordinary temperature. The resulting product is thoroughly washed with alcohol, and is found to be iodoxy-*m*-xylene, exploding at 193°.

0·0709 grm. gave 0·0627 grm. AgI; I = 47·12.
Calc. for $C_6H_3(CH_3)_2(IO_2)$—I = 48·11.

Iodoxy-o-*xylene*, $C_6H_3(CH_3)_2{}^{1\cdot2}(IO_2)^4$.—This compound has been prepared for the first time, since it was not known before. Yellowish crystals were obtained by treating iodo-*o*-xylene with concentrated chloric acid in the cold for several days. On washing with alcohol the substance is obtained pure. It explodes at 192—193°. The salt was analysed with the following result:—

0·0989 grm. gave 0·1310 CO_2 and 0·0817 grm. gave 0·0729 grm. AgI.
Calc. for $C_6H_3(CH_3)_2(IO_2)$ – C, 36·36; H, 3·41; I, 48·11.
Found—C, 36·18; H, 3·58; I, 48·9.

Iodoxy-mesitylene, $C_6H_2(CH_3)_3IO_2$.—This substance is obtained by keeping iodomesitylene for a few days in contact with strong chloric acid. The crystalline crude product thus obtained is washed with alcohol. It decomposes at 194°.

0·1415 grm. gave 0·1191 grm. AgI; I, 45·53.
Calc. for $C_6H_2(CH_3)_3IO_2$—I, 45·68.

Investigations on similar lines are being continued.—*Journal of the American Chemical Society*, xxxviii., No 5.

NOTES ON

THE COLORIMETRIC DETERMINATION OF PHOSPHORUS IN SOIL EXTRACTS.

By C. E. MILLAR and F. A. GANGLEP.

The colorimetric method for the determination of phosphorus, suggested by Veitch (*Journ. Am. Chem. Soc.*, 1903, xxv., 169) and perfected by Schreiner and Brown (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1463), has been used to some extent for a number of years. Little or no data where this method has been applied to soil solutions have been published, and the general feeling has prevailed that it was somewhat inaccurate in such work.

The writers were in need of a reliable method for determining small amounts of phosphorus in soil extracts, and consequently an investigation of this method was undertaken. A series of tests emphasised the precautions brought out by Veitch: (1) Use filter-paper as free of silica as possible, such as Schleicher and Schüll's No. 589. (2) Use exact amounts of nitric acid and molybdate solution. The use of a poorer grade of paper caused a reading almost double that obtained when blank determinations were run with the better paper. By varying the amount of nitric acid it was found that quite a distinct colour could be almost entirely dissipated. Varying amounts of molybdate solution also affect the colour.

With the greatest care in the purification and use of all reagents it was found impossible to get blank determinations without a trace of colour, and in consequence a small factor of correction was used.

The samples of soil were taken with a one-inch soil tube to a depth of three feet, every foot composing a separate sample. The samples were rubbed through a quarter-inch sieve and the soil thoroughly mixed by rolling in an oil cloth. The sample was then quartered with a large spatula and two 100-grm. samples weighed out. Each sample was obtained by taking portions from opposite quarters. Each 100-grm. sample was rubbed with 500 cc. of water for three minutes in a mortar. After standing for forty minutes the suspension was filtered in a Chamberland filter; 50 cc. of the filtrate were taken for analysis. This procedure gave two solutions from separate portions of a well mixed sample. The duplicates shown in Table I. are determinations on these separate solutions and do not represent determinations on different portions of the same solution.

TABLE I.—*Parts per Million* PO_4 *in Filtrates from Soils.*

Plot. No.	Depth. Feet.	PO_4 in duplicates.	
1.	1	3·00	3·00
	2	3·00	3·00
	3	3·00	3·50
2.	1	5·00	4·50
	2	3·50	4·00
	3	2·50	2·50
3.	1	2·50	2·50
	2	2·50	2·50
	3	1·50	1·50
4.	1	2·00	2·00
	2	2·00	2·00
	3	2·00	2·00
5.	1	1·00	1·00
	2	0·75	0·75
	3	1·00	1·25
6.	1	0·75	0·50
	2	1·00	1·00
	3	1·25	1·25
7.	1	2·00	2·50
	2	2·50	2·00
	3	2·00	2·00
8.	1	2·50	3·00
	2	2·00	2·50
	3	2·00	2·00
9.	1	2·50	2·50
	2	2·50	2·00
	3	2·50	2·50
10.	1	2·50	2·00
	2	2·50	2·50
	3	2·50	2·50
11.	1	1·25	1·25
	2	1·25	1·25
	3	1·50	1·50
12.	1	0·50	0·50
	2	0·50	0·50
	3	0·75	0·75
13.	1	0·00	0·00
	2	0·25	0·25
	3	0·50	0·50
14.	1	1·00	1·00
	2	1·25	1·25
	3	1·25	1·25

From Table I. it would appear that if sufficient care is given to the purity of reagents and to the measuring out of all reagents, determinations of small amounts of phosphorus may be made in soil extracts with considerable accuracy.—*Journal of Industrial and Engineering Chemistry*, vii., No. 7.

Interrelation of the Fossil Fuels.—The second number of vol. lv. of the *Proceedings of the American Philosophical Society, Philadelphia*, contains a lengthy paper by J. J. Stevenson on "The Interrelation of the Fossil Fuels." The author's aim was to ascertain how closely the fossil fuels, excluding petroleum, are related to each other in their physical and chemical characteristics, as well as in their modes of accumulation, and for this purpose he made personal examinations in almost all the coal regions of America, besides travelling widely in foreign countries. He also studied the literature of the subject, and has brought together a vast number of references to books, articles, and memoirs. The paper goes thoroughly into the question of the distribution and extent of peat deposits, the conditions necessary to its formation and its composition, and the tertiary coals or lignites are afterwards treated similarly, though somewhat more shortly.

NOTICES OF BOOKS.

The Paper Makers' Directory of All Nations. London: Dean and Son, Ltd. 1916. Pp. xlviii.+702+67. Price 10s. 6d. net.

This directory for 1916, which has just been published, contains a large amount of information which will be useful to all who are interested in the paper trade. It gives complete lists of the principal paper, pulp, and board mills of the world, the list of mills in enemy countries having been left as before the war, while in all other respects the information has been carefully checked and corrected. A comprehensive list of mill productions of all mills mentioned is included, giving the class of goods manufactured, the country of origin, and the names of the firms. The customary form and arrangement of the directory has been preserved, and it will be found indispensable to manufacturers and buyers of paper.

Some Properties of the Water in Coal. By Horace C. Porter and O. C. Ralston. Washington: Government Printing Office. 1916. Pp. 30. Price 5 cents.

This bulletin, which is Technical Paper No. 113 of the Bureau of Mines, deals with the manner in which water is held in coal, and how its properties and those of the coal are affected by the condition in which it is present. The thermal effect of wetting coal was studied by the authors experimentally, and the vapour pressures of the inherent water were also determined. The facts observed can all be readily explained on the colloid hypothesis—that part of the water in coal is held more tenaciously than free water by forces due to colloidal conditions. Thus, for example, this hypothesis explains the impossibility of drying coal completely in an atmosphere which is not perfectly dry, and also accounts for the very hygroscopic character of dry coal and the large changes in the percentage of moisture due to changes in the humidity of the atmosphere.

A Modern School. By Abraham Flexner. Occasional Paper No. 3. New York City: The General Education Board. 1916. Pp. 23.

This publication of the General Education Board is one of the occasional papers, which will be sent on request to anyone interested. It appears at an opportune moment, and will be appreciated by the many educationalists who are studying the state of secondary education in England and considering its future, especially with reference to the necessity for altering the curriculum. The opinions of the author are, in the main, in agreement with those which are being freely expressed in England nowadays. He considers that tradition plays far too large a part in determining the substance and purpose of current education. He believes that there should be a ruthless cutting out of many subjects which have been shown to serve no useful purpose in the education of the average student. Among these rejected subjects Latin and algebra appear to be the most important, for he thinks that a large number of students who devote a long time to the study of them get no grasp whatever of them. The ideal modern education should give a knowledge of the physical world and a knowledge of the social world, coupled with a power of attacking new problems with vigour and resource, and the author thinks that much could be done by omitting from the curriculum all useless subjects and building up a new course of work, in which the four main divisions would be science, industry, æsthetics, and civics.

The Training of Chemists. By Alexander Smith. Reprinted from *Science*, N.S., Vol. XLIII., No. 1114, May 5, 1916.

This Address was delivered at Urbana on the occasion of the opening of the chemical laboratory of the University of Illinois in April, 1916. In it the lecturer paid a glowing tribute to the spirit which had characterised the work of the University in chemistry, and congratulated the State upon its enterprise and success and upon the facilities offered by the new laboratory. The Address contained some very apposite remarks upon the question of the training of chemists, and teachers in this country could learn a good deal from its practical hints and suggestions. The lecturer commented upon the question of the courses of work suitable for the student in his first year at the University, and emphasised the need for training students so that they should be able to understand the chemistry and bio-chemistry of the future and not merely become acquainted with the facts and theories of the present day. He suggested that lecturing should be curtailed in favour of questioning the student, to give him practice in expressing his knowledge in words, to show that he had really assimilated what was put before him. His hints as to improved laboratory arrangement and the saving of waste by insisting upon care in the use of chemicals are thoroughly practical, and the adoption of some of his ideas would mean increased efficiency in many ways. Incidentally, the following startling figures of the ratio of chemists to population were given for different countries:—Switzerland, 300; Germany, 250; France, 7; Great Britain, 6; the number for the United States being in the lecturer's opinion nearer the last two than the first.

The People's Interest in Water-power Resources. By George Otis Smith. Washington: Government Printing Office. 1916. Pp. 8.

This lecture was delivered before the Second Pan-American Scientific Congress, Washington, December 28, 1915. The lecturer dealt with general considerations relating to the utilisation of flowing water, discussing the development of the source of power so as to meet present demands and the equitable division of the benefits of that development. He fully recognised the danger of monopoly as being greater than that of non-development, and discussed in some detail future possibilities in the United States and methods of control.

Reattivi e Reazioni. ("Reagents and Reactions"). By Dott. Prof. Edgardo Tognoli. Milan: Ulrico Hoepli. 1916. Pp. xii.+277. Price L. 3.50.

This little manual contains details of about 900 reagents which are commonly used in analytical chemistry, with instructions for carrying out all important reactions employed in such work. It will be found very useful to medical students and doctors and in bacteriological and microscopical work. Methods of testing reagents for purity are described, and many useful tables are included. The reagents and reactions are arranged alphabetically under the names of the authors first employing them, but an index of the names of the substances tested for is also given, so that there should be no difficulty in finding the reference to any desired test or reagent. The manual naturally lays no claim to originality, but it appears to be an accurate and well arranged compilation which will be welcomed by Italian chemists.

Cours de Manipulations de Chimie Physique et d'Electrochimie. ("Course of Practical Work in Physical Chemistry and in Electrochemistry"). By M. Centnerszwer. Paris: Gauthier Villars et Cie. 1914. Pp. vii.+182.

The text of this book is based upon the notes which were originally given to each student in the laboratory of physical chemistry of the Polytechnic Institute at Riga. The author's aim is primarily to facilitate the study of the laws of physical chemistry, and not merely to give a knowledge of the methods employed and some practice in the technique. In every chapter the laws which are under consideration are first stated, and discussed shortly but adequately from the theoretical point of view. These *résumés* will be found particularly useful to the beginner, giving him a summary of what he has read in more detailed works and consolidating his knowledge. The practical work is then described fully, the directions being sufficiently explicit for the student to be able to perform the experiments with but very little help from teacher or demonstrator. Finally, the methods of calculating results are explained, and the most important conclusions to be drawn are clearly stated. The general plan of the book follows that of Ostwald's classical Treatise on General Chemistry, and the author, who was a pupil of Ostwald's, acknowledges his debt to the great teacher and to his assistants. The Gas Laws are first treated, then the Properties of Liquids, Solutions, the Dynamics of Chemical Reactions, Thermochemistry, and, finally Electrochemistry, and the methods described are well chosen and should help to give the student a real working knowledge of the laws of Physical Chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 5, July 31, 1916.

Oxalates of Uranyl and Potassium.—A. Colani.— Three compounds of uranyl oxalate and potassium are known:—$K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$, $K_2(UO_2)(C_2O_4)_2 3H_2O$, $K_6(UO_2)_2(C_2O_4)_5 \cdot 10H_2O$. The study of the system water, oxalate of uranyl, and neutral oxalate of potassium at 15° and 50° has enabled the author to prepare these substances and determine the limits of their formation. He finds that an anhydrous salt, $K_2(UO_2)(C_2O_4)_2$, exists; its trihydrate is not formed at the ordinary temperature, but may exist below 50°.

No. 6, August 7, 1916. No. 7, August 14, 1916.

These numbers contain no chemical matter.

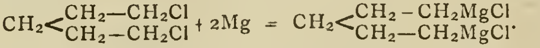
No. 8, August 21, 1916.

Action of Light upon Iodine and Iodised Water in an Aqueous Medium.—H. Bordier.— Iodised water is not a true solution, but the iodine is present in the water in the colloidal state. Iodide of starch is also in the colloidal state. When iodide of starch is exposed to the action of light it is completely decolorised, while the same liquid kept in darkness still possesses its colour. The blue coloration can be made to reappear by adding traces of iodine to the decolorised liquid. Iodised water in the same conditions loses its yellow colour, and the addition of starch gives no blue coloration although the control solution, kept away from the sun's rays, becomes blue at once. To explain these phenomena the following hypothesis may be put forward:—The particles of iodine in the colloidal state are charged with electricity, and hence their chemical properties are not identical with those of free iodine. The violet and ultra-violet radiations produce ionisation effects which in the end deprive the colloidal particles of their electric charges. These particles, when thus deprived of their charges, acquire chemical properties which they did not possess previously. For example, they could combine with the hydrogen of water to give hydriodic acid. Exactly the same thing happens with iodide of starch.

Bulletin de la Société Chimique de France. Vol. xix.-xx., No. 7, 1916.

Polymerisation of Ethylene.—M. de Montmollin.— It has frequently been remarked that the first member of the olefines, unlike the following terms of the series, cannot polymerise (condense). When ethylene is prepared by the action of phosphoric acid upon alcohol an oily substance appears and floats on the surface of the aqueous layer in the receiving vessel. This oily liquid, which is yellowish brown with a characteristic fluorescence, has been shown by the author to consist of a complex mixture of hydrocarbons, polymethylenic hydrocarbons predominating. After many fractionations he succeeded in obtaining from it the following:—Di-isopropyl, dimethyl diethyl methane, hexahydrometaxylene, hexhydroparaxylene. He also found that hexahydrocumene, decanaphthene, dodecanaphthene, and tetradecanaphthene are present.

Organo-magnesium Derivative of 1.5-Dichloropentane.—Enrique v. Zappi.—When magnesium acts upon ether and 1.5-dichloropentane the following reaction occurs:—



$$CH_2<\begin{matrix}CH_2-CH_2Cl\\CH_2-CH_2Cl\end{matrix}+2Mg = CH_2<\begin{matrix}CH_2-CH_2MgCl\\CH_2-CH_2MgCl\end{matrix}$$

Other secondary reactions also occur, involving the two substances in the molecular proportions 2:3, 3:4, and 4:5. The organo-magnesium compounds thus obtained when decomposed with water yield respectively cyclopentane, decane, pentadecane, and eicosane.

m-Phenetidine and some Derivatives.—Fréderic Reverdin and J. Lokietek.—When acetyl-*m*-phenetidine is nitrated, in general two mononitro compounds and one dinitro are obtained. Usually a mixture of the three substances, is the result, the mononitro compounds predominating, but by varying the conditions either the one or the other may be almost exclusively formed. To get the mononitro derivatives nitric acid ($D=1\cdot4$ or $1\cdot5$) is added to a solution of acetyl-*m*-phenetidine in acetic acid, the temperature being kept between 0 and 5° at first and then allowed to rise to about 30°. The product of the reaction is poured into ice-water and the precipitate thus obtained is filtered off after standing for a day. On boiling it with ligroin the chief product, 4-mononitro-*m*-acetyl phenetidine, is dissolved, while the less soluble residue is the isomer with the nitro-group at 6. When precipitated from ligroin the former is a yellowish flocculent compound from which almost pure white crystals are obtained by recrystallising in alcohol. The melting-point is 95°. The 6 isomer melts at 147°. The dinitro compound may be obtained by nitration of the mononitro derivatives, or by adding a mixture of *m*-acetyl phenetidine and potassium or sodium nitrate to sulphuric acid at 10° to 15°, and then pouring into ice-water. It is less soluble in alcohol than the mononitro derivatives, and crystallises from acetone or benzene in nearly colourless needles of melting-point 125°.

Derivatives of 2.6-Dinitro-benzyl-aniline.—S. Reich and M. Ghazarian.—When 2.6-dinitro-benzylaniline is reduced with tin and hydrochloric acid it is converted into a derivative of indazol, namely, nitro-phenyl indazol. If the reduction is effected by means of ammonium sulphide the product is 2-amino-6-nitro-benzylaniline, which reacts with hydrochloric acid and sodium nitrite to give nitro-phenyl-triazoline. The authors have shown that 2.6-dinitro-benzyl-acetaniline and 2.6-dinitrobenzyl-benzanilide both give amines on reduction.

MISCELLANEOUS.

Travancore Minerals Company, Limited.—The Public Trustee invites Tenders for the purchase of 10,000 Ordinary "A" Shares of £1 each, fully paid, and 19,998 7 per cent Cumulative Preference Shares of £1 each, 15s. paid, in Travancore Minerals Company, Limited. Particulars will be found in our advertisement columns.

Annual Report of His Majesty's Inspectors of Explosives.—The fortieth issue, for the year 1915, shows that, in spite of the very great increase recently in the manufacture of explosives and in the number of persons thus employed, the number of accidents has, on the whole, not increased unduly. Some modifications have been made in the laws relating to the manufacture of explosives, which are duly noted in the report. The chemical advisers draw special attention to the fact that explosives made with sodium nitrate are considerably less satisfactory than those made with the corresponding potassium salt; otherwise they have no special observations to make.

Industries of Organic Chemistry in France after the War.—In this article Prof. Alph. Mailhe discusses at length some important questions bearing on the development of the chemical industries in France after the war. He deals specially with dyes, synthetic perfumes, and pharmaceutical products, and gives a long historical account of the growth of the great German dyeing firms. He discusses the possibilities of fighting against German organisation, and shows that France possesses an abundance of the raw materials necessary for these industries, and that well-trained and efficient chemists should not be lacking in the future. He regards a very rigorous tariff as absolutely essential to keep out German goods, and emphasises the necessity for good travellers, well acquainted with foreign languages, to develope France's commerce. —*Revue Générale des Sciences*, No. 14, xxvii., 1916.

Liebig's Extract of Meat Co., Ltd.—The directors of Liebig's Extract of Meat Co., Ltd., have declared a half-year's dividend at the rate of 5 per cent per annum on the Preference Shares, payable less income tax at 5s. in the £, on and after October 2, to the proprietors who are registered on the 20th inst. In respect of Coupon No. 32 of the Preference Share Warrants to Bearer, such dividend, less income tax at 5s. in the £, will be payable on and after October 2 at the company's bankers, Messrs. Glyn, Mills, Currie, and Co., 67, Lombard Street, London, E.C.

New Laboratory Ozone Generator (Type 71).—This type of apparatus has been designed to permit of producing from air concentrations of ozone of a strength hitherto unobtainable. By its use as much as 16 grms. of ozone per cubic metre of air (or 8000 parts per million by volume) are readily obtained—or, in other words, about 6 per cent of the oxygen of the air can be ozonised, a figure which has never been attained with any other commercial ozone generator. The apparatus is constructed on the well-known Ozonair principle, offering a large cooling surface for the dissipation of the heat incidental to the generation of ozone. It is enclosed in a lead-lined containing tank, which is cooled by water for low concentrations, and preferably by a freezing mixture of ice and salt or other suitable material for the higher concentrations. Its capacity at the highest concentration is about 2½ litres of ozonised air per minute, but a much larger volume is available at lower concentrations. The use of oxygen instead of air, or a mixture of the two, is, of course, optional. The efficiency of the apparatus is very high for its size, being about 25 grms. of ozone per kilowatt at the high concentrations. The apparatus is supplied with a specially wound transformer (Type 82½), fitted with an additional high tension terminal, permitting of the widest range of regulation from the lowest to the highest concentrations. When an alternating current supply is not available it can be obtained by the use of a rotatory convertor which is operated by the continuous current supply. The convertor (Type 93) supplied with this set is designed for continuous working. It is fitted with ball-bearings, and will run for long periods without attention. A switchboard complete with main double pole switch and fuses, 5-point regulating switch for the transformer, and ammeter for indicating the current used, is a necessary part of the equipment. Where the electric current supply is continuous, a starting switch for the convertor must be added. For the purpose of accurate estimation a special test meter is furnished if desired. This meter measures very definitely the volume of air passed. The large dial is marked for a total of 10 litres divided into tenths of a litre, so that it is possible to measure with great accuracy. In addition to the centre dial there are three smaller dials to register a total of 10,000 litres. The dials can be graduated in cubic feet if specially ordered.

THE CHEMICAL NEWS

Vol. CXIV., No. 2967.

ADDRESS TO THE PHYSIOLOGICAL SECTION OF THE BRITISH ASSOCIATION.

Newcastle-on-Tyne, 1916.

By Prof. A. R. CUSHNY, M.A., M.D., F.R.S.,
President of the Section.

On the Analysis of Living Matter through its Reactions to Poisons.

I am told that the chair of Section I has not been held by a pharmacologist for many years, and I wish to express the pleasure I feel in the honour that has been done me personally, and even more in the recognition vouchsafed to one of the youngest handmaidens of medicine. Pharmacology has too often shared the fate of the bat in the fable: when we appeal for support to the clinicians we are told that we represent an experimental science, while when we attempt to ally ourselves with the physiologists we are sometimes given the cold shoulder as smacking too much of the clinic. As a matter of fact we should have a footing in each camp, or, rather, in each division of the allied forces. And the more recent successes in the application of pharmacology to diseased conditions are now beginning to gain it a rather grudging recognition from clinicians, while the alliance with the biological sciences is being knit ever more closely. The effect of chemical agents in the living tissues has assumed a new and sinister aspect since the enemy has resorted to the wholesale use of poisons against our troops, but I must leave this for the discussion to-morrow.

I wish to day to discuss an aspect of pharmacological investigation which has not been adequately recognised even by the pharmacologists themselves and which it is difficult to express in few words. In recent years great advances have been made in the chemical examination of the complex substances which make up the living organism, and still greater harvests are promised from these analytic methods in the future. But our progress so far shows that while general principles may be reached in this way, the chemistry of the living organ, like the rainbow's end, ever seems as distant as before. And, indeed, it is apparent that the chemistry of each cell, while possessing general resemblances, must differ in detail as long as the cell is alive. No chemistry dealing in grammes, nor even microchemistry dealing in milligrammes, will help us here. We must devise a technique dealing with millionths to advance towards the living organism. Here I like to think that our work in pharmacology may perhaps contribute its mite; perhaps the action of our drugs and poisons may be regarded as a sort of qualitative chemistry of living matter. For chemical investigation has very often started from the observation of some qualitative reaction, and not infrequently a good many properties of a new substance have been determined long before it has been possible to isolate it completely and to complete its analysis. For example, the substance known now as tryptophane was known to occur in certain substances and not in others long before Hopkins succeeded in presenting it in pure form. And in the same way it may be possible to determine the presence or absence of substances in living tissues, and even some of their properties, through their reaction to chemical reagents, that is, through the study of the pharmacology of these tissues. A simple example may render the point clearer: It is possible that if the toxicity of the saponins to different cells were accurately known, the relative importance of the lecithins in the life of these cells might be estimated, and this might give a hint to the chemist in approaching their analysis. I do not claim that pharmacological investigation can at present do much more than the qualitative testing of the tyro in the chemical laboratory, but even a small advance in the chemistry of living matter is worthy of more attention than this has received hitherto.

All forms of living matter to which they have free access are affected by certain poisons, and some of these have obvious chemical properties which suggest the method of their action; thus the effects of alkalis and acids and of protein precipitants hardly need discussion. Others, such as quinine and prussic acid, which also affect most living tissues, have a more subtle action. Here it is believed that the common factor in living matter which is changed by these poisons is the ferments, and quinine and prussic acid may therefore be regarded as qualitative tests for the presence of some ferments, notably those of oxidation, and, in fact, have been used to determine whether a change is fermentative in character or not. Formaldehyde was stated by Loew to be poisonous to living matter through its great affinity for the NH_2 group in the proteins, a suggestion which has perhaps not received enough attention of late years, during which the importance of this group in proteins has been demonstrated. The toxicity of other general poisons, such as cocaine, is more obscure. But what has been gained already in this direction encourages further investigation of the action of the so-called general protoplasm poisons and further efforts to associate it with the special constituents of the cell.

In other poisons the action on the central nervous system is the dominating feature, and among these the most interesting group is that of the simple bodies used as anæsthetics and hypnotics, such as ether, chloroform, and chloral. The important use of this group in practical medicine has perhaps obscured the fact that they act on other tissues besides the central nervous system, though we are reminded of it at too frequent intervals by accidents from anæsthesia. But while they possess this general action, that on the nervous tissues is elicited more readily. Not only the nerve-cell, but also the nerve-fibre react to these poisons, as has been shown by Waller and others. And even the terminations are more susceptible than the tissues in which they are embedded, according to the observations of Gros. The selective action on the nervous tissues of this group of substances has been ascribed by Overton and Meyer to the richness in lipoid substances in the neurons, which leads to the accumulation of these poisons in them, while cells containing a lower proportion of lipoid are less affected. In other words, Overton and Meyer regard these drugs as a means of measuring the proportion of lipoids in the living cell. This very interesting view has been the subject of much discussion in recent years, and, in spite of the support given it by several ingenious series of experiments by Meyer and his associates, no longer receives general acceptance. Too many exceptions to the rule have to be explained before the action of these bodies can be attributed wholly to their coefficients of partition between lipoids and water. At the same time the evidence is sufficient to justify the statement that the property of leaving water for lipoid is an important factor in the action of the bodies, although other unknown properties are also involved in it. And whatever the mechanism of the characteristic action, these substances in certain concentrations may be regarded as tests for the presence of nervous structures and have been employed for this purpose.

Other bodies acting on the nervous system have a much narrower sphere. Morphine and strychnine, for example, appear to be limited to the region of the nerve-cells, but there is still doubt whether they affect the cell-body alone or the synapses between certain of its processes. They have not been shown to act on peripheral nervous structures in vertebrates, nor on any but specific regions of the central nervous system. Nor has it been established that they affect invertebrates. The substance with which they react is obviously limited by very narrow boundaries around the nerve-cell.

More interest has been displayed in recent years in the alkaloids which act on the extreme terminations of various groups of nerves. These are among the most specific reagents for certain forms of living matter which we possess. Thus, if an organ reacts to adrenaline, we can infer that it contains the substance characteristic of the termination of sympathetic fibres with almost as great certainty as we infer the presence of a phenol group from the reaction with iron. And this sympathetic substance can be further analysed into two parts by means of ergotoxine, which reacts with the substance of the motor sympathetic ends, while leaving that of the inhibitory terminations unaffected. Similarly the endings of the parasympathetic nerves are picked out with some exceptions by the groups represented by atropine and pilocarpine, and here again there must be some definite substance which can be detected by these reagents.

Further, some light has been thrown on, at any rate, one aspect of these nerve-end substances by the observation that they all react to only one optical isomer in each case. Thus the dextro-rotatory forms are ineffective in both atropine and adrenaline, and this suggests strongly that the reacting body in the nerve-ends affected by these is itself optically active, though whether it bears the same sign as the alkaloid is unknown. This very definite differentiation between two optical isomers is not characteristic of all forms of living matter. For example, the heart muscle seems to react equally to both lævo- and dextro-camphor. The central nervous system contains substances which react somewhat differently to the isomers of camphor and also of atropine, but the contrast is not drawn so sharply as that in the peripheral nerve-ends.

Another test alkaloid is curarine, the active principle of curare, which in certain concentrations selects the terminations of the motor nerves in striated muscle as definitely as any chemical test applied to determine the presence or absence of a medal.

The tyro in the chemical laboratory is not often fortunate enough to be able to determine his analysis with a single test. He finds, for example, that the addition of ammonium sulphide precipitates a considerable group of metals, which have then to be distinguished by a series of secondary reactions. The pharmacologist, as an explorer in the analysis of living matter, also finds that a single poison may affect a number of structures which appear to have no anatomical or physiological character in common. But as the chemist recognises that the group of metals which react in the same way to his reagent have other points of resemblance, so perhaps we are justified in considering that the effects of our poison on apparently different organs indicate the presence of some substance or of related substances in them. A great number of instances of this kind could be given, and in many of these the similarity in reaction extends over a number of poisons, which strengthens the view that the different organs involved have some common reacting substance.

One of the most interesting of these is the common reaction of the ends of the motor nerves in striated muscle and of the peripheral ganglia of the autonomic system. It has long been known that curare and its allies act in small quantities on the terminations of the motor nerves in ordinary muscle, while larger amounts paralyse conduction through the autonomic ganglia. More recently it has been developed by the researches of Langley that nicotine and its allies, acting in small quantities on the ganglia, extend their activities to the motor ends in large doses. Some drugs occupy intermediate positions between nicotine and curare, so that it becomes difficult to assign them to either group. These observations appear to leave no question that there is some substance or aggregate ommon to the nerve-ends in striated muscle and to the autonomic ganglia. As to the exact anatomical position of this substance, there is still some difference of opinion. Formerly it was localised in the terminations of the nervous fibres in the muscles and ganglia, but Langley has shown that in the latter the point of action lies in the ganglion-cell itself, and his researches on the antagonism of nicotine and curare in muscle appear to show that the reacting substance lies more peripherally than was supposed, perhaps midway between the anatomical termination of the nerve and the actual contractile substance. Another analogy in reaction has been shown to exist between the ganglia and the terminations of the post-ganglionic fibres of the parasympathetic, for Marshall and Dale have pointed out that a series of substances, such as tetramethyl-ammonium, affect each of these in varying degrees of intensity. The specific character of the reaction is shown by the fact that while it is possessed by the tetramethyl-ammonium salts, the tetraethyl ammonium homologues are entirely devoid of it.

Another close relationship is shown by the reaction of the glucosides of the digitalis series on the heart and vessels. These all act on the muscle of the heart, and in higher concentration on that of the vessel-walls. There must therefore be a common base in these which is affected by the drugs. And the existence of this is perfectly intelligible in view of the fact that the heart is developed from the vessels. A more obscure relationship is shown by the reaction of this group to the inhibitory cardiac centre in the medulla, which is thrown into abnormal activity by their presence in the blood, as has been shown alike by clinical and experimental observations. A similar relation is shown by the common reaction of the heart-muscle and the vagus centre to aconitine and some other related alkaloids. On the other hand, the saponin series, which shows a closer relationship to the digitalis bodies in the heart-muscle, is devoid of its characteristic action on the medulla. The reacting substance in the heart is thus capable of responding to digitalis, saponin, and aconitine, while that in the vagus centre can associate only the first and last and is not affected by the saponins; the common reactions indicate that the two are related, while the distinctive effect of saponin shows that they are not identical. A similar relationship may be drawn from the action of morphine and the other opium alkaloids on pain sensation, on respiration, and on the movements of the alimentary tract. Exact determinations of the relative power of these alkaloids in these regions are not at our disposal as yet, but sufficient is known to suggest that while morphine affects a common substance in the medullary centre and the intestinal wall, the other members of the series act more strongly in one or other position.

It was long ago pointed out that caffeine affects both kidney and muscle-cell, and Schmiedeberg has attempted to correlate the intensity of action of the purine bodies at these points and to measure the probable diuretic action by the actually observed effect on the contraction of muscle. Other reactions of the kidney suggest a relationship to the wall of the bowel. For example, many of the heavy metals and some other irritant bodies act strongly on the kidney and bowel, and again, according to one view of renal function, many of the simple salts of the alkalis affect the kidney in exactly the same way as the bowel-wall. This last may, however, be due to the physical properties of the salts, and the likeness in reaction to those of kidney and bowel, which is striking enough, may arise from a likeness in function of the epithelium rather than from any specific relationship to the salts which is not common to other forms of living matter.

Many other examples might be cited in which organs which are apparently not related, either morphologically or in function, react to poisons in quantities which are indifferent to the tissues in general. And this reaction in common can only be interpreted to mean that there is some substance or group of related substances common to these organs. The reaction may differ in character; thus a drug which excites one organ to greater activity may depress another, but the fact that it has any effect whatever on these organs in preference to the tissues in general indicates some special bond between them, some quality which is not shared by the unaffected parts of the body. I have, therefore, not differentiated between excitation and depression in discussing this relation. One is tempted to utilise the nomenclature introduced by Ehrlich here and to state that the common reaction is due to the presence of haptophore groups while the nature of the reaction (excitation or depression) depends on the character of the toxophore groups. But while these terms may be convenient when applied to poisons whose chemical composition is altogether unknown, they merely lead to confusion when the question concerns substances of ascertained structure. Thus, as Dale has pointed out, it is impossible to suppose that such substances as tetramethyl-ammonium and tetraethyl ammonium owe the difference in reactions to specific haptophore groups in the one which are absent in the other. It seems more probable that in this instance and in others the difference in the effect of these bodies in the tissues arises from differences in the behaviour of the molecule as a whole than in differences in the affinities of its special parts; that is, that the action of these poisons is due to their physical properties rather than to their chemical structure, although this, of course, is the final determining cause.

In the same way the common reaction of tissues, which I have so far ascribed to their possessing some substance in common, may arise from community of physical relationship, and I wish to avoid the implication borne by the word "substance," which I have used in the widest sense, such as is justified perhaps only by its historical employment in theological or philosophical controversy. The reaction of living tissue to chemical agents may arise from a specific arrangement in its molecule, but may equally be attributed to the arrangement of the molecules themselves. And the curious relationships in the reactions of different tissues may indicate, not any common chemical factor, but a common arrangement of the aggregate molecules. We are far from being able to decide with even a show of probability which of these alternatives is the correct one, and my object to-day has been to draw attention to these relationships rather than to attempt their elucidation. Hitherto the speculative pharmacologist has been much engaged in comparing the chemical relationship of the drugs which he applies to living tissues; much useful knowledge has been incidentally acquired, and the law has been formulated that pharmacological action depends directly on, and can be deduced from chemical structure. This view, first elaborated in this country, has in recent years shared the fate of other English products in being advertised from the housetops and practically claimed as the discovery of more vociferous investigators. On examining the evidence, old and new, one cannot help feeling that attention has been too much directed to those instances which conform to the creed, while the far more numerous cases have been ignored in which this so-called rule fails. The difficulties are very great; for example, what chemical considerations can be adduced to explain why the central nervous tissues react differently to bromide and chloride, while to the other tissues these are almost equally indifferent; or how can the known chemical differences between potassium and sodium be brought into relation with the fact that they differ in their effects in almost every form of living tissue?

Less attention has been paid to the other factor in the reaction, the properties of the living tissue which lead one cell to react to a poison while another fails to do so. I have pointed out some curious relations between different organs, but much needs to be done before any general view can be obtained. Further detailed examination of the exact point at which poisons act, and much greater knowledge of the physical characters of the drugs themselves and of the relation of colloid substances to these characters, are needed. We must attempt to classify living tissues in groups not determined by their morphological or even functional characters, but by their ability to react to chemical agents. Advance is slow, but it is continuous, and if no general attack on the problem is possible as yet, our pickets are at any rate beginning to give us information as to the position of the different groups to be attacked. And when a sufficient number of these qualitative reactions have been ascertained for any form of living matter, it may be possible for some Darwin to build a bridge from the structural chemistry of the protein molecule to the reactions of the living cell. We can only shape the bricks and mix the mortar for him. And my purpose to-day has been to indicate how the study of the effects of drugs on the living tissue may also contribute its mite towards the great end.

ADDRESS TO THE BOTANICAL SECTION OF THE BRITISH ASSOCIATION.

By A. B. RENDLE, M.A., D.Sc., F.R.S., President of the Section.

Since our last meeting the Great War has continued to hold chief place in our lives and thoughts, and in various ways, and to a greater or less degree, has influenced our work. In the case of many Botany has had for the time being to be set aside, while others have been able to devote only a part of their time to scientific work. On the other hand, it is gratifying to note that some have been able to render helpful service on lines more or less directly connected with their own science. The trained botanist has shown that he may be an eminently adaptable person, capable, after short preparation on special lines, of taking up positions involving scientific investigation of the highest importance from the standpoints of medicine and hygiene,

We have to regret the loss of a promising young Cambridge botanist, Alfred Stanley Marsh, who has made the supreme sacrifice for his country. Happily, in other cases lives have been spared, and we are able to welcome their return to the service of botany.

In common with our fellow-botanists throughout the world, we have learned with sorrow of the death of one of the kindliest and most versatile exponents of the science, Count Solms Laubach, whom we have welcomed in years past as a guest of our Section.

May I also refer to the recognition recently given by the Royal Society to the services of two of our Colonial botanists? Mr. W. H. Maiden, of Sydney, who has done so much in Australia for the development of botany and its applications in his position as Government Botanist and Director of the Botanic Gardens at Sydney, and whose kindness some of us have good cause to remember on the occasion of the visit of this Association to Sydney in 1914, and Professor W. H. Pearson, of Cape Town, who is doing useful work of botanical exploration in South-West Africa.

A little more than two years ago, during the enforced but pleasant leisure of our passage across the Indian Ocean to Australia, I was discussing with our President for the year the possibility of a war with Germany. He was confident that sooner or later it was bound to come. I was doubtful. "But what will prevent it?" asked my companion. "The common sense of the majority," was my reply. He was right and I was wrong, but I think he was only less surprised than myself when next evening we heard, by wireless, rumours of the outbreak of what rapidly developed into the great European war. But even a few weeks later, when Germany was pressing westwards, and the very existence of our Empire was threatened, we hardly began to appreciate what it would mean, and we still talked of the possibility of an International Botanical Congress in 1915.

We know more now, and I need not apologise for considering in my Address the part which botanists can take in the near future, especially after the war. For one thing at least is certain, we are two years nearer the end than when it began, and let us see to it that we are not as backward in preparing for post-war as we were for war problems.

Some months ago the various Sectional Committees received a request to consider what could be done in their respective Sections to meet problems which would arise after the war. Your Committee met and discussed the matter, with the result that a set of queries was sent round to representative botanists asking that suggestions might be presented for consideration by the Committee. A number of suggestions were received of a very varied kind, indicating that in the opinion of many botanists at any rate much might be done to utilise our science and its trained workers in the interests of the State and Empire. Your Committee decided to arrange for reports to be prepared on several of the more important aspects by members who were specially fitted to discuss these aspects, and these will be presented in the course of the meeting. These reports will, I am convinced, be of great value, and may lead to helpful discussion; they may also open up the way to useful work.

For my own part, while I might have preferred to consider in my Address some subject of more purely botanical interest, I felt that under the circumstances an academic discourse would be out of place, and that I too must endeavour to do something to effect a more cordial understanding between botany and its economic applications.

For many of us this means the breaking of new ground. We have taken up the science because we loved it, and if we had been able to shed any light on its numerous problems the work has brought its own reward. But some of us have on occasion been brought into touch with economic problems, and such must have felt how inadequate was our national equipment for dealing with some of these. In recent years we have made several beginnings, but these beginnings must expand mightily if present and future needs are to be adequately met, and if we are determined to make the best use of the material to our hand.

Whether or no we have been living for the past forty years in a fools' paradise, it is certain that our outlook will be widely different after the war, and may the stimulus of a changed environment find us ready to respond!

Sacrifice must be general, and the botanist must do his bit. This need not mean giving up the pursuit of pure science, but it should mean a heavy specialisation in those lines of pure science which will help to alleviate the common burden, will render our country and the Empire less dependent on external aid, and knit more closely its component parts.

It may be convenient to consider, so far as they are separable, Home and Imperial problems.

Without trenching on the domain of Economics, we may assume that increased production of foodstuffs, timber, and other economic products will be desirable. The question has been raised as to the possibility of increasing at the same time industrial and agricultural development. But as in industry perfection of machinery allows a greater output with a diminished number of hands, so in agriculture and horticulture perfection of the machinery of organisation and equipment will have the same result.

There are three factors in which botanists are primarily interested—the plant, the soil, and the worker.

The improvement of the plant from an economic point of view implies the co-operation of the botanist and the plant-breeder. The student of experimental genetics, by directing his work to plants of economic value, is able, with the help of the resources of agriculture and horticulture, to produce forms of greater economic value, kinds best suited to different localities and ranges of climate, those most immune to disease and of the highest food-value. Let the practical man formulate the ideal, and then let the scientist be invited to supply it. Much valuable work has been done on these lines, but there is still plenty of scope for the organised Mendelian study of plants of economic importance. It is a very large subject, and we are hoping to hear more about it before we separate.

A minor example occurs to me. Do the prize vegetables which one sees at shows and portrayed in the catalogues represent the best products from an economic point of view; in other words, is the standard of excellence one which considers solely their value as foodstuffs? A chemico-botanical examination would determine at what point increase in size becomes disproportionate to increase in food-value, and thus correct the standard from an economic point of view. And, presumably, the various characters which imply greater or less feeding value offer scope for the work of the Mendelian.

The subject of intensive cultivation offers a series of problems which are primarily botanical. It would be a useful piece of investigation to work out the most profitable series which can be grown from year to year with the least expenditure on manures and the minimum of liability to disease. A comparatively small area would suffice for the work.

The introduction of new plants of economic value is within the range of possibility; our repertoire has increased in recent years, but an exhaustive study of food plants and possible food plants for man and stock would doubtless yield good results. It is matter of history that the introduction of the tea plant into further India was the result of observations by Fortune, a botanical collector. The scientific botanist may find pleasant relaxation in the smaller problems of horticulture.

We have heard much lately as to the growing of medicinal plants, and experience would indicate that here is opportunity for investigation, and, unless due care is taken, also danger of waste of time, money, and effort. A careful systematic study of species, varieties, and races is in some cases desirable in order to ensure the growth of the most productive or valuable plant, as in the case of the Aconites; and such a study might also reveal useful substitutes or additions. Here the co-operation between the scientific worker and the commercial man is imperative. I have recently been interested to hear that the special properties of medicinal plants are to be subjected to experiment on Mendelian lines.

During the past year there has been considerable activity in the collecting of wild specimens of various species of medicinal value, frequently, one fears, involving loss of time and waste of plants, owing to want of botanical or technical knowledge and lack of organisation. In this connection a useful piece of botanical work has recently been carried out by Mr. W. W. Smith, of Edinburgh, on the collection of sphagnum for the preparation of surgical dressings. The areas within the Edinburgh district have been mapped and classified so as to indicate their respective values in terms of yield of sphagnum. By the indication of the most suitable areas, the suitability depending on extent of area, density of growth, freedom of admixture of grass or heather, as well as facility of transport and provision of labour, the report is of great economic value. The continuity of supply is an important question, and one which should be borne in mind by collectors of medicinal plants generally. And while it is not the most favourable time to voice the claims of protection of wild plants, one may express the hope that the collector's zeal will be accompanied by discretion.

The advantages arising from a closer co-operation between the practical man and the botanist is illustrated by the research laboratories recently organised by the Royal Horticultural Society at Wisley. Such an institution forms a common meeting-ground for the grower of plants and the botanist. The former sets the problems, and the latter takes them in hand under conditions approaching the ideal, and with the advantages of mutual discussion and criticism. Institutions such as these will give ample opportunity to the enthusiastic young botanist who is anxious to embark on work of investigation. The student of plant physiology will find here work of great interest. The grower has perforce gained a great deal of information as to the behaviour of his plants under more or less artificial conditions, but he is unable to analyse these conditions, and the co-operation of the physiologist is an invaluable help. Experiments in the growth of plants under the influence of high-tension electricity are at the present time being carried out at Wisley. Such experiments may be conducted anywhere where land and power are available, but it is obviously advantageous that they should be conducted by an expert plant-physiologist versed in scientific method and not directly interested in the result. Dr. Keeble's recent series of lectures on Modern Horticulture at the Royal Institution deal with matter which is full of interest to the botanist. For instance, he shows how the work of Continental botanists on the forcing of plants has indicated methods in some cases simple and inexpensive, which have proved of considerable commercial value, and that there is evidently scope for work in this direction, which, while of interest to the plant-physiologist, may be also of general utility.

The subject of the soil offers problems to the botanist as well as to the chemist and proto-zoologist. In the plant we are dealing with a living organism, not a machine; and an adequate knowledge of the organism is essential to a proper study of its nutrition and growth. The facility with which a considerable sum of money was raised just before the war to improve the equipment at Rothamsted, where work was being done on these lines, indicates that practical men are ready to come forward with financial help if work which promises to yield results of economic importance is being seriously carried out. And it is significant of the attitude of botanists to such problems that there is only one trained botanist on the staff of this institution.

The study of manures and their effect on the plant should attract the botanist as well as the chemist. It this connection I may refer to Mr. Martin Sutton's recent work at Reading on the effects of radio-active ores and residues on plant-life. A series of experiments was carried out in two successive years with various subjects selected for the different character of their produce, and including roots, tubers, bulbs, foliage, and fruit. From the immediate point of view of agriculture and horticulture the results were negative; the experiments gave no hope of the successful employment of radium as an aid to either the farmer or gardener. Speaking generally, the produce from a given area was less when the soil had been treated with pure radium bromide, or various proprietary radio-active fertilisers, than when treated with farmyard manure or a complete fertiliser; while the cost of dressing was very much greater. To quote Mr. Sutton's concluding words, "The door is still open to the investigator in search of a plant fertiliser which will prove superior to farmyard dung or the many excellent artificial preparations now available." But though the immediate result was unsatisfactory to the grower, there were several points of interest which would have appealed to the botanist who was watching the course of the experiments, and which, if followed up, might throw light on the effect of radium on plant-life and lead in the end to some useful result. As Mr. Sutton points out, many of the results were "contradictory," while a close examination of the trial notes, together with the records of weights, will furnish highly interesting problems. For instance, there was evidence in some cases that germination was accelerated by presence of radium, though subsequent growth was retarded, and the fact that in several of the experiments plants dressed with a complete fertiliser in addition to radium have not done so well as those dressed with the fertiliser only may be regarded as corroborating M. Truffaut's suggestion that radium might possess the power of releasing additional nitrogen in the soil for the use of plants, and that the plants in question were suffering from an excess of nitrogen. Certain remarkable variations between the duplicate unmanured control plots in several of the experiments led to the suggestion that radium emanations may have some effect, apparently a beneficial one. I have quoted these experiments as an example of a case where the co-operation of the botanist and the practical man might lead to useful results, and at the same time afford work of much interest to the botanist.

As an introduction to such work university professors might encourage their advanced students to spend their long vacation in a large nursery or botanic garden where experimental work is done.

As regards the worker in agriculture and horticulture, how can the botanist help? Apart from well-staffed and well-equipped schools of agriculture and horticulture, which require the botanist's assistance, a wider dissemination of the botanist would be advantageous. Properly trained botanists distributed through the country with their eyes open might be a valuable asset in the improvement of production; botanist and cultivator might be mutually helpful; the former would meet problems at first hand, and the latter should be encouraged by the co-operation. A kind of first-aid class suggests itself, run by a teacher with a good elementary knowledge of botany, upon which has been erected a general knowledge of horticultural operations. This would afford a vocation for students of scientific bent who cannot spare the time for a long university course. Some of us may remember the courses, arranged by various County Councils thirty years or so ago, financed by the whiskey money, out of which have grown some useful permanent educational institutions. But these courses were often barren of result, owing partly to insufficient "sympathy" between the lecturer and his audience. A young man fresh from the university who was waiting for a more permanent job was brought into touch with the practical man in the lecture hall, and the contact was, so to speak, not good. Between the two was a gulf across which the lecturer shouted, and his words often conveyed little meaning to those on the other side. A great deal of money must have been spent with incommensurate results.

On the other hand, we must be careful to work economically and not wear out high-class tools on rough work. I think there is some danger of this in connection with certain courses in horticulture for women. Girls who have had a good general education enter, at the age of seventeen or eighteen, on a course of study, lasting for two or three years, of horticultural methods and the kindred sciences. So far, good; but after all this training the finished product should aspire to something more than market gardening in competition with the man who left school at twelve or fourteen, has learnt his business practically, and has a much lower standard of living.

The utilisation of waste lands is a big subject and trenches on the domain of Economics. But important botanical problems are involved and careful ecological study will prepare the way for serious experimental work. The study of the growth of plants in alien situations is fraught with so many surprises and apparent contradictions that successful results may be looked for in most unlikely situations. I remember a striking instance near Lake Tarawera, in the North Island of New Zealand. The area in question had been completely devastated in the great eruption of Mount Tarawera in 1886, the ground being covered with ash to a depth of several feet. When I saw it two years ago the vegetation of a considerable area was almost purely Central European. The trees were poplar, *Robinia*, and elder, with an undergrowth of dog-rose, bramble, &c. I was not able to find out the recent history of the locality and there were very few signs of habitation, but it was not the kind of vegetation one would expect to find growing so naturally and freely in such a locality. But the subject of utilisation of waste lands will occupy us later.

The study of the diseases to which plants are liable, and their prevention and cure, offers a wide and increasing field for inquiry, and demands a larger supply of trained workers and a more definite and special system of training.

For the study of those which are due to fungi it is obviously essential that a thorough general knowledge of fungi and laboratory methods should be acquired, preferably at some Pathological Institution which would also be in touch with the cultivator and naturally approached by those requiring advice and help in connection with disease, on the same principle that a medical school is attached to a hospital. An important part of the training should be the study of the disease in the field and the conditions under which it arises and flourishes. From the point of view of Mycology much useful scientific work remains to be done on the life history of the fungi which are or may be the causes of disease. The study of preventive methods must obviously be carried out in the field, and, while these are mainly mechanical processes, they need careful supervision; the question of the subsequent gathering and disposal or a crop must not be overlooked. Experiments in the use of dust instead of spray as a preventive of fungous and insect attack have recently been carried out in America. Other plant diseases afford problems for the physiologist, who is a necessary part of the equipment of the Pathological Institute.

The anatomical and chemical study of timbers might with advantage occupy a greater number of workers. The matter is of great economic importance. Questions of identity are continually arising, and in the present vague state of our knowledge it is often difficult or impossible to give a satisfactory answer. Samples of timber are put on the market shipped, say, from West Africa under some general name such as mahogany; the importer does not supply leaves and flowers for purpose of identification. and in the present incomplete state of our knowledge it is often impossible to make more than a vague attempt at determination. Or a merchant brings a sample which has been sent from X as Y, which it obviously is not; but what is it, whence does it probably come, and what supply of it is likely to be forthcoming? These are questions which it would be useful to be able to answer with some greater approach to accuracy than at present. And it should be the work of definitely trained persons. I recall a sample of wood which some months ago, coming from a Government Department, went the round of the various institutions which were at all likely to be able to supply the required information as to its identity. It should have been matter of common knowledge where to apply, with at the same time reasonable certainty of obtaining the information required.

It is possible also that a more systematic study of minute structure would help to solve questions of affinity. A chemical study has proved of value in the discrimination of the species of *Eucalyptus* in Australia.

Apart from co-operation between the botanist and the practical or commercial man, there is need for co-ordination between workers. I give the following incident from real life. At the meeting of an advisory committee the head of a certain institution stated that he had set one of his staff to work at a certain disease which was then under discussion, but had learnt shortly after that a student at another institution was engaged on the same piece of work. A conference led to a useful division, one of the workers to study the life history of the organism in the laboratory, the other to work at conditions of life, &c., in the field. But it also transpired that another institution, as well as another independent worker, were engaged on the same problem, and while it was suggested that in one case co-operation might be invited, it was deemed inadvisable to approach the other. The problem in this case was not one of such special difficulty as to require so much attention, and even if it had been some co-ordination between the various working units would have been helpful. Similar instances will occur to you. The measure of efficiency of our science should be the sum of the efficiency of its workers. It should be possible to devise some means for informing fellow-workers as to the piece of work in hand or proposed to be undertaken, and thus on the one hand to avoid wasteful expenditure of time and effort, and not infrequently the hurried publication of incomplete results, and on the other to ensure where practicable the benefits of co-operation.

The various illustrative suggestions which I have made would imply a close co-operation between the schools of botany and colleges and institutions of agriculture, horticulture, and forestry; to pass from the former to one of other of the latter for special work or training should be a natural thing. While on the one hand a University course is not an essential preliminary to the study of one or other of the applied branches, the advantages of a broad, general training in the principles of the science cannot be gainsaid. The establishment of professorships, readerships, or lectureships in economic botany at the University would supply a useful link between the pure and applied science, while research fellowships or scholarships would be an incentive to investigation.

There is the wider question of a rapprochement between the man of science and the commercial man. Its desirability is obvious, and the advantages would be mutual; on the one hand it would secure the spread and application of the results of research, and on the other hand the man of science would be directed to economic problems of which otherwise he might not become cognisant. The closer association between the academic institution and those devoted to the application of the science would be a step in this direction.

Our British possessions, especially within the tropics, contain a wealth of material of economic value which has been only partially explored. One of the first needs is a tabulation of the material. In the important series of Colonial floras incepted by Sir Joseph Hooker, and published under the auspices of Kew, lies the foundation for further work. Consider, for instance, the "Flora of Tropical Africa," now rapidly nearing completion. This is a careful and, so far as possible with the material at hand, critical descriptive catalogue of the plants from tropical Africa which are preserved in the great British and European Herbaria. The work has been done by men with considerable training in systematic work, but who know nothing at first hand of the country the vegetation of which they are cataloguing. Such a "Flora" must be regarded as a basis for further work. Its study will indicate botanical areas and their characteristics, and suggest what areas are likely to prove of greater or less economic value, and on what special lines. It will also indicate the lines on which areas may be mapped out for more detailed botanical exploration. That this is necessary is obvious to any botanist who has used such a work. A large proportion of the species, some of which may, on further investigation, prove to be of economic value, are known only from a single incomplete fragment. Others, for instance, which may be of known economic value, doubtless exist over much larger areas and in much greater quantity than would appear from the "Flora." The reason of these shortcomings is equally obvious. The collections on which the work is based are largely the result of voluntary effort employed more or less spasmodically. The explorer working out some new route, who brings what he can conveniently carry to illustrate the plant products of the new country; the Government official or his wife, working during their brief leisure or collecting on the track between their different stations; the missionary or soldier, with a penchant for natural history; to these and similar persons we are largely indebted for additions to our knowledge of the plant life. Advantage has sometimes been taken of a Government expedition to which a medical man with a knowledge of or taste for natural history, or, in rare cases, a trained botanist, has been attached.

The specimens brought home by the amateur collector often leave much to be desired, and little or no information is given as to precise locality or the nature of the locality, the habit of the plant, or other items of importance or interest. There may be indications that the plant is of economic value, but no information as to whether it is rare or plentiful, local or occurring over a wide area.

Samples of wood are often brought, but generally without any means of identification except a native name; and it must be borne in mind that native names are apt to be misleading; they may be invented on the spur of the moment to satisfy the white man's craving for information or when genuine are often applied to more than one species.

A large proportion of the more extensive collections are due to German enterprise, and the best representation of this work is naturally to be found in Germany, though it is only fair to state that the German botanists have been generous in lending material for work or comparison. The botanical investigation of German East Africa and the Cameroons has been carried out by well-trained botanists and collectors, and the results of their work published both from botanical and economic points of view. I may refer to the large volume on German East Africa, which contains not only a general account of the vegetation and a systematic list of the genera and species comprising the flora, but also an account of the plants of economic value classified according to their uses. The exploration of the Belgian Congo has been seriously undertaken by the Belgian Government, and a number of large and extensively illustrated botanical memoirs have been issued. Some of us may be familiar with the fine Congo Museum near Brussels.

It is time that pioneer work gave place to systematic botanical exploration of our tropical possessions, and the preparation of handy working floras and economic handbooks. Work of botanical exploration should be full of interest to the young botanist. But if he is to make the best use of time and opportunity he must have had a proper course of training. After completing his general botanical course, which should naturally include an introduction to the principles of classification, he should work for a time in a large Herbarium, and thus acquire a knowledge of the details of systematic work and also of the general outlines of the flora of the area which he is to visit later. He should then be given a definite piece of work in the botanical survey of the area. From the collated results of such work convenient handbooks on the botanical resources of regions open to British enterprise could be compiled. There will be plenty of work for the systematist who cannot leave home. The ultimate elaboration of the floristic work must be done in the Herbarium with its associated library.

There is also need of a careful monographic stndy of genera of economic value which would be best done by the experienced systematist at home, given a plentiful supply of carefully collected and annotated material. An example of such is the systematic account of the species of *Sanseviera* by Mr. N. E. Brown, recently issued at Kew. Closely allied species or varieties of one and the same species may differ greatly in economic value, and the work of the monographer is to discover and diagnose these different forms, and elucidate them for the benefit of the worker in the field.

If we are to make the best use of our resources botanical research stations in different parts of the Empire, adequately equipped and under the charge of a capable trained botanist, are a prime necessity. We seem to have been singularly unfortunate, not to say stupid, in the management of some of our tropical stations and botanical establishments.

The island of Jamaica is one of the oldest of our tropical possessions. It is easy of access, has a remarkably rich and varied flora, a fine climate, and affords easy access to positions of widely differing altitude. It is interesting to imagine what Germany would have made of it as a station for botanical work if she had occupied it for a few years. The most recent account of the flora which pretends to completeness is by Hans Sloane, whose work antedates the Linnæan era. A flora as complete as available material will allow is now in course of preparation in this country, but the more recent material on which it is based is due to American effort. Comparatively recently a mycologist has been appointed, but there is no Government botanist to initiate botanical exploration or experimental work or to advise on matters of botanical interest. A botanical station ideal for experimental work in tropical botanical problems is a mere appendage of a Department of Agriculture, the Director of which is a chemist.

A botanical station for research to be effective must be under the supervision of a well-trained botanist with administrative capacity, who must have at his disposal a well-equipped laboratory and ground for experimental work. He must not be expected to make his station pay its way by selling produce or distributing seedlings and the like; a botanical station is not a market-garden. The Director will be ready to give help and advice on questions of a botanical nature arising locally, and he will be on the look-out for local problems which may afford items of botanical research to visiting students. Means must be adopted to attract the research student, aided if necessary by research scholarships from home. The station should have sufficient Imperial support to avoid the hampering of its utility by local prejudice or ignorance. The permanent staff should include a mycologist and a skilled gardener.

The botanical station does not preclude the separate existence of an agricultural station, but the scope of each must be clearly defined, and under normal conditions the two would be mutually helpful. Nor should the botanical station be responsible for work of forestry, though forestry may supply problems of interest and importance for its consideration.

Finally, I should like to suggest the holding of an Imperial Botanical Congress at which matters of general and special interest might be discussed. The visit of the British Association to Australia was, I think, helpful to the Australian botanists; it was certainly very helpful and of the greatest interest to those coming from home. Many of the addresses and papers were of considerable interest and value, but of greater value was the opportunity of meeting with one's fellow-workers in different fields, of conversation, discussion, and interchange of ideas, the better realisation of one's limited outlook and the stimulus of new associations. A meeting which brought together home botanists and botanical representatives from oversea portions of our Empire to discuss methods of better utilising our vast resources would be of great interest and supremely helpful. Let us transfer to peace purposes some of the magnificent enthusiasm which has flowed homewards for the defence of the Empire in war.

In this brief Address I have tried, however imperfectly, to indicate some lines on which botanists may render useful service to the community. To a large extent it means the further development and extension of existing facilities added to an organised co-operation between botanists themselves and between botanists and the practical and commercial man; this will include an efficient systematic cataloguing of work done and in progress. We do not propose to hand over all our best botanists to the applied branches and to starve pure research, but our aim should be to find a useful career for an increasing number of well-trained botanists, and to ensure that our country and Empire shall make the best use of the results of our research. Incidentally, there will be an increased demand for the teaching botanist, for he will be responsible for laying the foundations.

Complaint has been made in the past that there were not enough openings for the trained botanist; but if the responsibilities and opportunities of the science are realised we may say, rather, "Truly the harvest is plentiful, but the labourers are few." Botany is the *alma mater* of the applied sciences, agriculture, horticulture, forestry, and others; but the *alma mater* who is to receive the due affection and respect of her offspring must realise and live up to her responsibilities.

ANALYSIS BY MACHINERY.

By ERIC SINKINSON,
Demonstrator in Technical Analysis in the Imperial College of Science and Technology, South Kensington.

In the department of analytical chemistry little has been devised to lighten the manipulative requirements of the chemist. Every operation undertaken requires the utmost skill and patience, whilst often the time expended is out of all proportion to the results obtained.

The wash-bottle—the chemist's staff—is ever in his hand, which, when so occupied, is not free for any other operation.

The washing of precipitates is one of the greatest time-absorbing factors in the laboratory. Yet there is no escape from it, demanding as it does the utmost attention and skill; in this way the output of a laboratory is considerably limited.

With a view to minimising the loss of time, and thus increasing the scope of the chemist, the machine is illustrated in Fig. 1.

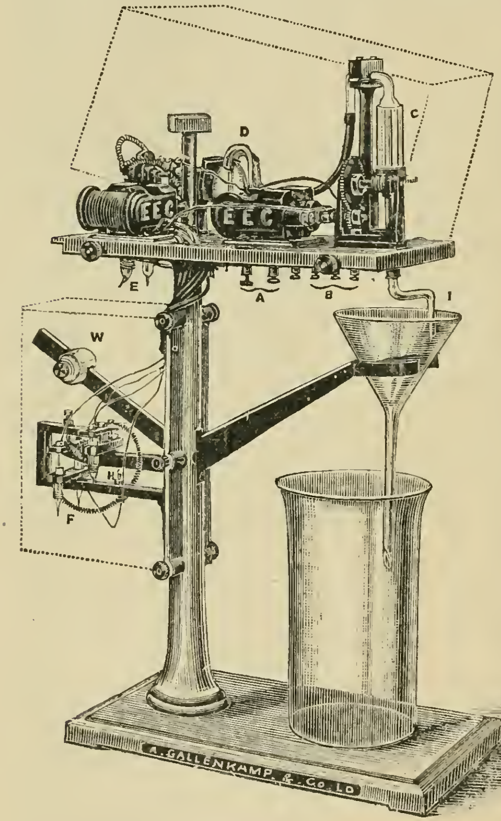


Fig. 1.

After thorough and severe tests it has shown itself capable of satisfying this long-felt want, and hence is worthy of the notice of analysts. The machine can carry out quite automatically the washing of any precipitate in a more efficient way than can be done by hand. The constructional details are set out briefly in the following:—The apparatus intrinsically is a balance, on one arm of which is fixed a supporting ring for a filter funnel, on the other a movable counterpoise weight and also an electrical commutator. Over the beam is fixed a table carrying two electric motors, shown in diagram as B and C in Fig, 2, one to control through a specially constructed mercury valve (A and B, Fig. 3) the flow of water to a jet which is rotated by the other motor. The two motors are connected to the current supply through the commutator arm A, Fig. 2, in such a way that when the funnel end of the beam is up the water supplied by gravity flow from a flask or tin-lined copper tank, which may be heated if necessary, passes freely to the jet which sprays the water round the edge of the paper containing the precipitate to be washed reposing in the funnel.

The counterpoise weight at the other end of the beam, which is regulated by a screw, is moved into such a position that when sufficient water has flowed into the funnel the increased weight causes the beam to drop, thus shutting off the water supply to the jet, so that no current is wasted during the period it is not required.

As the water drips from the funnel the arm supporting it becomes lighter, the beam rises, and water again enters the filter through the rotating jet. In this manner the washing process continues until it is complete.

The valve controlling the water supply to the jet is a glass bulb, shown in Fig. 3, containing mercury represented in the figure by shading, fitted with an inlet tube C, which reaches to the bottom of the bulb, and an outlet tube D. When the bulb is in an upright position, as in A, Fig. 3, the water supplied to it cannot flow on account of the resistance of the mercury to it. If the valve be turning through 90°, as in B, Fig. 3, the mercury rolls away from the inlet tube, thus allowing the water a free passage to the outlet D.

This bulb is mounted on the machine in such a way that the motor B (Fig. 2), which is reversible, will turn it from the horizontal to the vertical plane and *vice versa*, as the commutator arm A is raised or lowered. In order to check the rotation of the motor in either direction after it has turned over the valve, it is cut out of circuit by a turn of the wheel O, fixed to the valve on which are mounted two steel contacts, P and R, Fig. 2, capable of alternately dipping into the mercury cups, H and J, so that whilst one is out of circuit contact is made in the other ready for the return journey as soon as the commutator moves over.

The apparatus is simple in construction, robust, and with few moving parts. The electric contacts are made by steel rods dipping into steel mercury cups carried on ebonite insulators. The working parts are enclosed from dust and chemical fumes by suitable covers, and when in use appears as in Fig. 1.

If it should be required to wash a precipitate, with a predetermined quantity of wash-water, say 200 cc., a small float can be arranged, attached to a cut-out on the main circuit to the apparatus, and this will arrest the washing quite automatically when the amount of water has passed through the filter.

Six or twelve of these machines can be mounted together for use in laboratories where a considerable portion of the analyst's time is consumed, as in steel and refractory materials laboratories, in this laborious operation of filter-washing.

The current, which is only intermittently used, that is when water is being sprayed into the filter, can be taken from the main power or lighting circuit.

The machine shown in the accompanying illustration is actuated by a pressure of 240 volts in conjunction with a suitable resistance. If, however, electric power or lighting is not laid on in the particular laboratory in which the apparatus is to work, a pressure of eight volts from an accumulator is sufficient to control it.

The apparatus thus becomes to the chemist a companion of the first order. It gives him a means of completely and effectively washing precipitates with the minimum quantity of hot or cold water in the shortest possible time. As the complete apparatus may be covered during the process of washing dust can be excluded and the contents of the filter-paper left uncontaminated. The machine may be left to complete a washing after the laboratory is closed down for the night.

In conjunction with this machine a decanting apparatus, the details of which may be communicated later, can be

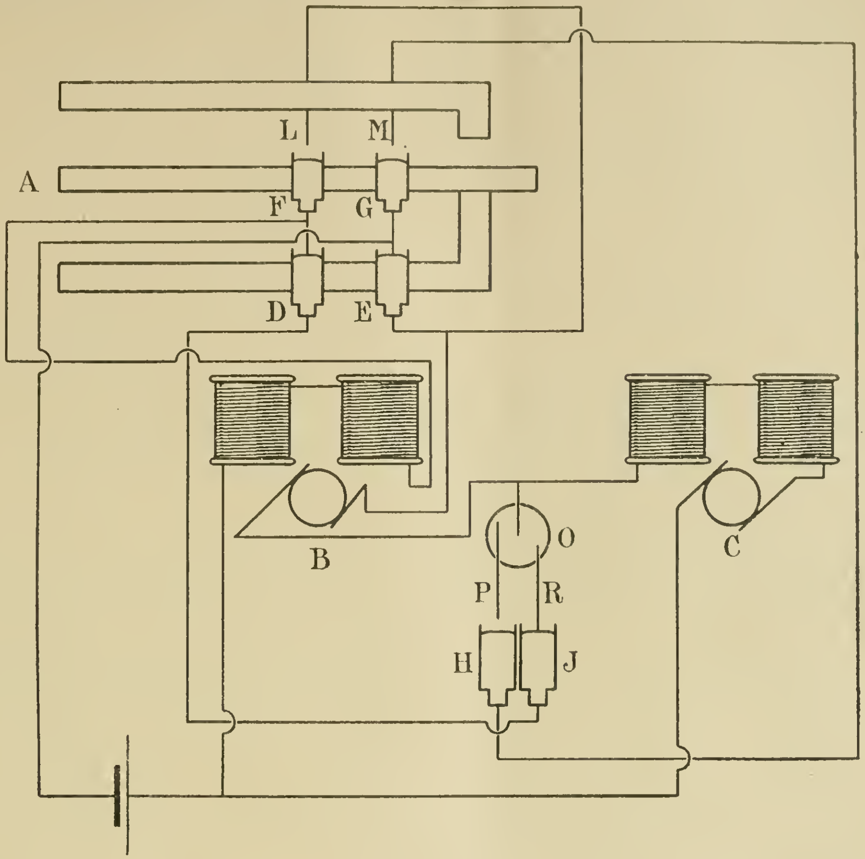

L
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Fig. 2.

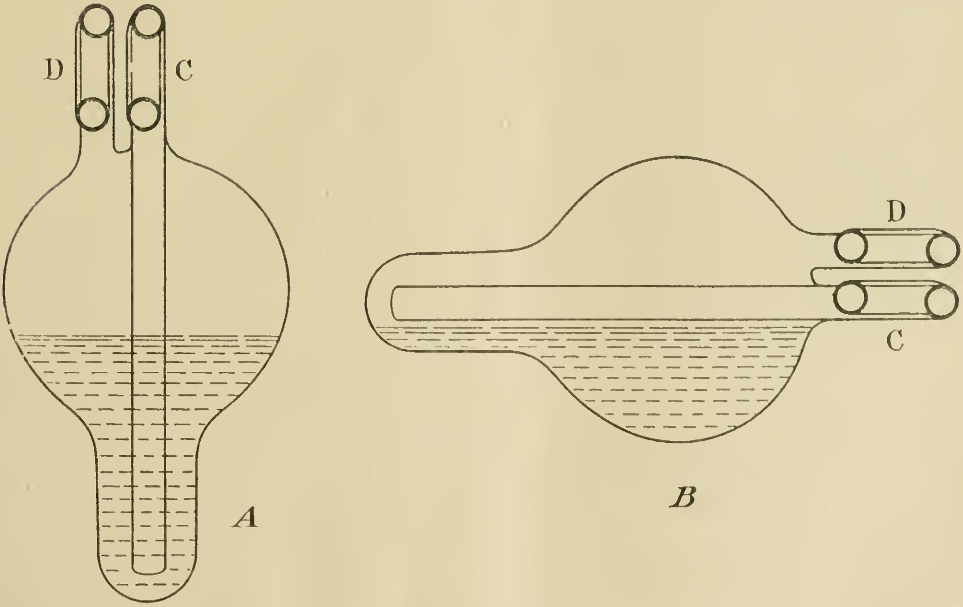

Fig. 3.

used, so that large bulks of liquid may be automatically decanted through the filter paper. This apparatus is of especial value in agricultural laboratories, where much time is spent in this operation.

It is hoped that this brief account may interest readers in an endeavour to minimise some of the time-absorbing operations of the analytical laboratory.

I should like to express my thanks to Messrs. A. Gallenkamp and Co. for the loan of the electro of the block (Fig. 1) used in the illustration.

THE FRUIT OF *SMILAX ROTUNDIFOLIA*.

By CELIA ROGERS.

The fruit of the *Smilax rotundifolia*, common greenbriar, was gathered at different places in the vicinity of Mount Vernon, Iowa, during October, 1915. The fruit consists of berries which grow on bushes from 4 to 6 feet in height in low heavy soil, usually in a wild undergrowth in the woods. The berries are not edible. They grow in compact clusters from 1½ to 2 inches in diameter. They are dark in colour and resemble the wild grape. The single berry is about one-fourth of an inch in diameter, perfectly round, and contains four hard brown seeds. The average weight when dried is 0·1195 grm. The fruit is not juicy, and there is very little loss of weight from drying.

The Sugar.

We placed 150 grms. of the dried fruit in a litre flask attached to an upright condenser, and treated on the hot water-bath with alcohol for twelve weeks. A fresh portion of alcohol was added every few days. Distilled water was then substituted for alcohol, and digestion was continued for eight weeks. The sugar was determined from the two extractions by the use of Fehling's solution. A cc. of the extract was evaporated to dryness to remove the alcohol; it was diluted to 50 cc. with distilled water, and while boiling was titrated with Fehling's solution. We found the sugar to be 7½ per cent of the dried fruit. A portion of the sugar extract was digested some hours on the water-bath with bone-black. By the phenylhydrazine test as outlined by Sherman and Williams (*Journ. Am. Chem. Soc.*, xxviii., 629) fracture was present. Tests for dextrine gave unsatisfactory results.

The Oils.

The residue of the portion from which the sugar was extracted was dried and weighed. This was placed in a 16 ounce flask, fitted with an inverted condenser, and the oils were separated after digesting with ether four or five weeks. The oils were purified by digesting the ether solution a number of hours with bone-black on the water-bath. To determine the specific gravity 2 cm. were measured out accurately, and it was found to be 0·8585. The saponification equivalent by the Koettstorfer method was found to be 357·14. Rape oil is 350·67. The specific gravity as we determined it is somewhat too low for rape oil.

The Ash.

We added five different portions. From the first the silica, iron and alumina, calcium, and magnesium were determined; from the second SO_3; from the third the manganese; from the fourth the phosphate; from the fifth the alkalis. The last were determined by the J. Lawrence Smith method as found in Knight's "Quantitative Analysis."

In ashing the fruit, the odour resembles that of burning leaves. It required a comparatively long time, due to the hardness of the seeds. The average weight of ash was 3·06 per cent of the dried fruit.

The substances found in the ash were the following:—

Silica	0·08	per cent
Fe_2O_3 and Al_2O_3 ..	17·60	„
CaO	0·79	„
MgO	0·24	„
SO_3	7·92	„
Mn	0·76	„
P_2O_5	13·38	„
KCl	32·38	„
$NaCl$	5·28	„
Total	78·43	„

There was some CO_2 also unburned carbon in the ash.

Nitrogen and Proteins.

These were determined by the Kjeldahl-Dunning method. We found 1·12 per cent of nitrogen, equivalent to 7 per cent of proteins in the dried fruit. We found citric and tartaric acids present in rather small quantities, but did not determine the amount.

We desire to express our thanks to Dr. N. Knight for suggestions in carrying forward the work.

REFINING VEGETABLE AND ANIMAL OILS.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.,
Professor of Chemistry and Director of the Laboratory, College of the City of New York, Member of the Institute.

The terms "fat" and "wax" are commonly applied, more or less indiscriminately, to solid substances which have a greasy feeling to the touch and do not dissolve in water. Physically waxes are regarded as having generally a harder consistency than fats. Chemically fats are usually compounds of the trihydric alcohol, glycerol, $C_3H_5(OH)_3$, while the waxes are compounds of monohydric alcohols of large molecular weight; for example, cetyl alcohol, $C_{16}H_{33}OH$, myristic alcohol, $C_{30}H_{61}OH$, and cholesterol, $C_{27}H_{45}OH$. The names applied to some of these substances do not lessen the confusion; for example, "wool fat" and "spermaceti" are compounds of cholesterol and cetyl alcohol, hence are in reality waxes, while "Japan wax," a compound of glycerol, is actually a fat.

A fat, such as is indicated above, has among other physical properties a characteristic melting-point. Those which are liquid at ordinary temperatures are called *oils*. It is of such substances more especially that this communication deals, although reference will be made to cocoanut oil, which may or may not be a solid at ordinary temperatures, therefore technically might be regarded as a fat.

It will be understood that the term "oil" as here used is not to be associated with the natural or petroleum oils, *i.e.*, hydrocarbon oils, or the essential oils, both classes of which in general exhibit in a way the physical but not the chemical properties, necessarily, referred to above.

Fats are widely distributed in the vegetable and animal kingdoms, and, referring to the former only for the time being, we may say they are primarily glycerides of oleic, palmitic, and stearic acids. These fats are found *mainly* but not necessarily in the reproductive bodies, such as spores and seeds. They are found in spores, sexual and asexual, of many algæ. In angiosperms they are widely distributed, replacing wholly or in part carbohydrates as reserve food material, and they are often associated with protein reserves; for example, in the seed from which colza oil, palm oil, cotton-seed oil, linseed oil, olive oil, and cocoa butter are obtained. It is present, perhaps, as a reserve food material, associated with starch, in some tubers. The starch in the parenchyma of the stem of certain plants may be converted into fat during the winter's cold, and *vice versa* when there is a rise of temperature in the summer time. Without venturing into the misty etiology involved we may for our purposes realise the likelihood of the presence of carbohydrates, proteins, and other substances derived therefrom, as gums, &c., in oils obtained from these sources by the various means to be referred to later.

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* From the *Journal of the Franklin Institute*, June, 1916. Presented at a meeting of the Section of Physics and Chemistry, held February 10, 1916.

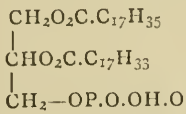
These oil-containing bodies invariably contain some colouring matter. Some of the colouring matters appear to be essential for certain of the changes just referred to. The most prominent pigment appears to be chlorophyll, an ester of tricarboxylic acid, chlorophyllin,

$$C_{31}H_{39}N_4Mg(COOH)_3,$$

and is the normal green colouring matter of plants. It may easily be broken down into substances that contain magnesium and substances that do not contain that metal.

Accompanying the chlorophyll are several pigments more or less insoluble in the cell sap—namely, carotin ($C_{40}H_{56}$), yellow to red in colour, and xanthophyll ($C_{40}H_{56}O_2$), a neutral body, yellow to orange in transmitted light. These substances may be destroyed by the action of such powerful chemical agents as concentrated sulphuric acid, especially if heated in the presence of oxygen.

Closely related to the fats is a group of substances known as phosphatides or lecithins. Occurring in egg-yolk to about 9 per cent we find them to the extent of from 0·25 to 1·75 per cent in cereals and leguminous seeds; hence they appear in the oils extracted from the seed. They are glycerol esters, two of the acidities being neutralised by fatty acids, the third being saturated by a combination of phosphoric acid and choline, as shown here—



$$\begin{array}{l} CH_2O_2C.C_{17}H_{35} \\ | \\ CHO_2C.C_{17}H_{33} \\ | \\ CH_2—OP.O.OH.O.C_5H_{13}N,OH \end{array}$$

It is easily broken up by lipase and hydrolysed by boiling with alkalis and acids.

We always also find a small quantity of unsaponifiable residue in fats, which is in the main composed of the monohydric alcohols, cholesterol, $C_{27}H_{45}OH$, and phytosterol, the latter now being a generic term for a group of allied substances, with formulæ varying from $C_{27}H_{45}OH$ (sitosterol) to $C_{30}H_{47}OH$ (stigmosterol). Chlolesterol occurs in the bile, brain, and blood of animals, and is the chief alcohol constituent of wool-fat. All vegetable fats contain phytosterol, the amount varying from 0·1 to 0·3 per cent, being even higher in the oil obtained from certain peas and beans, especially Calabar beans.

The oils are extracted by disintegration of the mass involving a disruption of the oil-sacs:—(*a*) with a suitable solvent; (*b*) rendering by heat, with or without water; (*c*) or pressure, mechanical, applied when the mass is cold or hot.

If the mass extracted be selected and perfectly clean and fresh the oil or fat obtained is usually neutral and "sweet." The exigencies of commercial operation do not admit of these conditions, however, so the oil or fat produced is usually acid and more or less contaminated. The contaminations may be quite normal and natural. They may be bacterial in nature and also contain the very interesting substances known as enzymes (lipase, for example) which induce hydrolysis; that is to say, they will cause any water present to disintegrate the fats (and other bodies) into simpler bodies. This may be facilitated by exposure to air and light, so that a freshly expressed oil that is sweet may soon acquire an unpleasant taste and odour. In some cases we say it becomes rancid, but in all cases the oil develops acidity, and the amount of the acidity of a particular oil is a function of time.

Under favourable conditions—and they are usually favourable—these changes take place within the oil-containing bodies, so that freshly produced oil is usually acid, which acidity increases on keeping. The enzymes are "killed," or decomposed, or at least their directive activity ceases, when they have been exposed to a temperature of about 200° C. It has not been considered a good procedure by the practitioners of the art of oil extraction and refining, however, to heat the oil to such a temperature immediately after its production, but I venture the opinion that the increased development of acidity in crude oil in storage or in transit to a refinery will be materially affected by such treatment. However, it will be necessary to be assured that substances charred or scorched at that temperature are absent.

As mentioned above, oils and fats are primarily glycerides of the saturated palmitic ($C_{16}H_{32}O_2$) and stearic ($C_{18}H_{36}O_2$) acids, associated with the fatty acids of several unsaturated series. For example:—

1. Oleic acid, $C_{18}H_{34}O_2$, type $C_nH_{2n-2}O_2$.
2. Linolcic acid, $C_{18}H_{32}O_2$, type $C_nH_{2n-4}O_2$.
3. Linolenic acid, $C_{18}H_{30}O_2$, type $C_nH_{2n-6}O_2$.
4. Clupanodonic acid, $C_{18}H_{28}O_2$, type $C_nH_{2n-8}O_2$.
5. Ricinoleic acid, $C_{18}H_{34}O_3$, type $C_nH_{2n-2}O_3$.

The last is an hydroxy acid, which undergoes a particular polymerisation under suitable conditions.

Most fatty oils on exposure to the air tend to thicken, due partly to oxidation and partly to polymerisation, or both. Oils are in fact classified by many according to their drying qualities and tendency toward resinification. These properties play an important part in their utilisation in the arts, and their treatment in refining is materially affected by the time which may have elapsed from actual production to their refining. For example, a freshly produced linseed oil may be profitably refined by a process which is inapplicable if the oil be "aged oil."

Oil as stated is normally a liquid, and we usually associate the phenomena of solution with a liquid. To be sure, this is a restricted conception, but will answer for our purposes. In this connection oil acts like water as a fluid. Water in motion carries fine particles suspended through long distances and deposits them in time, when fairly quiet, as we know from the formation of alluvial soils. Water carries certain substances in solution. These latter substances are sometimes coloured and are partly fixed on the filter when that water passes through certain filtering media. For instance, we are able to adsorb Congo red from a water solution with filter-paper. Again, water carries certain substances which do not stop on the filter; they are invisible and show themselves only when we apply the ultra microscope. These finely divided substances, not small enough to be in actual solution, will remain suspended in the water for long periods of time. They are called colloids. By various means, through heat, addition of an acid, an alkali or a salt, by the influence of an electric current, or by the addition of other colloids, these very finely divided substances may be caused to agglomerate; that is, they may be converted into particles of sufficient size to be separated from the fluid by means of a filter. Exactly the same is true of oils. Organic colloid solutions may be viscous; the liquid particles are suspended in a liquid medium.

Many of the contaminating substances, referred to here in general, may be suspended in the oil, may be in solution in the oil, or may be in a colloidal condition in the oil.

It will, therefore, be quite apparent that crude vegetable and animal oils contain a variety of impurities traceable to a great variety of causes. The character of the crude oil depends not only upon the kind and part of the vegetable (wood, nut, seed, &c.) and animal (fish, whale, &c.) used, but the quality of the raw material at the time of expressage or extraction (rusting, rotting, fermentation, sprouting, heating, &c.), the method followed, the care exercised in the process, and the conditions to which the oil is subjected prior to its refining. In many cases, in fact, we find metallic soaps present in the crude oil, which soaps have resulted from an interaction of decomposition products of the oil and the rendering vessels.

No universal method for refining animal and vegetable oils is known. Your forbearance will not be taxed, however, even were it profitable, in discussing all the various proposals for fitting these oils best to the several purposes experience and practice have shown them to be applicable. A number of processes have been proposed, patented, or kept secret during the last 125 years. Around the knowledge and power of the practical oil-refiner not a little mystery still obtains. Each individual oil presents its own problem, and even the same oil by name, obtained under different conditions, involves judgment, based on the knowledge of the chemistry involved, to secure the best and most economical results. Furthermore, the use to which the oil is to be put must be considered; for example, one wants acid oil for some paints and neutral oils for foods.

(To be continued).

MISCELLANEOUS.

The Faraday Society.—The Society will hold a General Discussion on "Refractories" at their first autumn meeting, the date of which is provisionally fixed for Wednesday, November 8, 1916. The Discussion will be presided over by Sir Robert Hadfield, F.R.S., President of the Society, and the opening paper will be read by Dr. J. W. Mellor, of Stoke-on-Trent. Suggestions are invited from those specially interested in the subject as to any particular aspects which they would like ventilated or discussed, and those who are desirous of contributing to the Discussion or who wish to show any exhibit at the Meeting, are invited to communicate with Mr. F. S. Spiers, Secretary of the Faraday Society, 82, Victoria Street, Westminster, S.W.

Chemical Industries of France.—In the conclusion of a series of articles upon this subject which has been appearing in the *Revue des Produits Chimiques* (Nos. 4—15, 1916) the following table appears:—

Production in Kgrms. per head of Population.

Product.	United States.	Germany.	England.	France.
Sulphuric acid . ..	22·0	23·0	27·0	25·0
Soda	6·75	7·85	16·3	8·25
Ammonium sulphate	1·55	7·85	10·0	1·7
Superphosphates ..	32·48	26·00	19·00	48·00
Chloride of lime ..	0·9	1·0	2·67	0·625
Calcic cyanamide ..	0·64	0·493	—	0·187
Zinc	3·08	3·98	1·35	1·585
Copper	5·89	0·59	1·21	0·3
Lead	4·07	2·6	0·71	0·7
Aluminium	0·225	0·043	0·174	0·45
Nickel	—	0·071	0·121	0·05
Tin	—	0·177	0·43	0·012

The author lays great stress upon the importance of providing further facilities for professional instruction in France, pointing out that nine-tenths of the young generation gets none at all. He suggests that it may be necessary to make it compulsory. He believes that in the future the chemist will begin to take his proper place in the national life, and that the outlook for the establishment of a prosperous and vigorous chemical industry in France is excellent.

Oxidising Ferment in the Grey Matter.—Horacio Damianovich.—There exists in the grey matter of the cerebrum, cerebellum, and medulla one or more substances which cause the oxidation of the alkaline mixture of paraphenylene diamine and naphthol, and the alkaline solution of phenolphthaleïn. In general characters (destruction of the oxidising power by heat, acids, &c.) the substance resembles the ferments known as oxidases, which are insoluble in water and soluble in electrolytes. It appears to belong to the globulins. There is a certain parallelism between the oxidising activity of the ferment and the activity of the nervous system.—*Anales de la Sociedal Quimica Argentina*, No. 13, iv., 1916.

Dextrorotatory Chlorhydrate and Bromhydrate of Pinene. Dextrorotatory Camphene (Austra-camphene).—D. E. Tsakalotos and B. Papaconstantinon.—Wallach pointed out that pinene chlorhydrate shows a peculiarity as regards its optical properties. While from lævorotatory essence of terebenthene lævorotatory pinene chlorhydrate is obtained, an *inactive* chlorhydrate is obtained from dextrorotatory essence of terebenthene. He stated that pinene bromhydrate presents the same optical anomalies. The authors have prepared for the first time the following dextrorotatory compounds, and determined their principal constants:—

	α_D.
d-Chlorhydrate of pinene ..	+33·19
d-Bromhydrate of pinene ..	+31·31
d-Camphene	+84·05

They used essence of terebenthene from Greece, and they found that the optical anomaly observed by Wallach is not exhibited by the derivatives of dextrorotatory pinene extracted from it.—*Journal de Pharmacie et de Chimie*, August 16, 1916, xiv., No. 4.

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THE CHEMICAL NEWS

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ADDRESS TO THE ECONOMIC SCIENCE AND STATISTICS SECTION OF THE BRITISH ASSOCIATION.

Newcastle-on-Tyne, 1916.

By Prof. A. W. KIRKALDY, M.A., B.Litt., M.Com.,
President of the Section.

When the British Association held its meeting in Australia in August, 1914, the war cloud had only just burst, and thus the distinguished economist who occupied the Presidential Chair of this Section could deal freely with the normal economic problems of old and young communities, disregarding the new and disastrous problems resulting from a great world war. Last year, however, my predecessor was compelled to take account of the critical events of the preceding twelve months. The war which so many presumably well-informed people expected to be over in less than a year is still with us, and the economic difficulties have increased in number and intensity. It is true that one of our statesmen has declared that the war may end sooner than some of us think—a not very hopeful utterance, but still I feel warranted from various signs in dealing in this Address rather with the period of reconstruction after the war than with the existing situation, for, owing to kaleidoscopic changes, what is written as to present conditions in August will probably be quite out of date by September, whilst the work of reconstruction may last for the best part of a century, and continue to affect the well-being of the community throughout succeeding history.

Some Thoughts on Reconstruction after the War.

We have been at war for two years, and the war has been waged more strenuously than any that human history records. It used to be said that a great European war under modern conditions could not last more than six months; but this prediction, like so many other preconceptions, has been falsified by a world calamity that to the great mass of mankind was entirely unforeseen.

In every sphere this great war has worked, and will yet work, great changes, but in the economic sphere the effects that can already be noted far exceed those in any other.

Up to the present the man in the street will tell you that the war has cost us over £2,000,000,000. In mentioning that sum he probably thinks of sacks of sovereigns, a printing-press feverishly turning out Treasury notes, and the various devices with which he is familiar for making currency or credit. But it would probably sound strange to him to hear that the number of sovereigns in the country is, if anything, greater than when the war commenced, and that currency generally has been enormously increased during the past twenty-four months, for it is not currency that has been consumed. The same man in the street, especially if he live in a munitions district, will discover that there is money in plenty in circulation, that the people all look well-to-do and are living as they seldom or never have before, and he may conclude that war is, after all, not such a bad thing—at any rate, it brings prosperity.

What is the truth? When we say that the war has cost £2,000,000,000 we mean that we have consumed that amount of commodities and services, that we have diverted capital and labour into new channels of production, but that these channels, unlike those connected with a good scheme of irrigation which may make the wilderness to blossom like the rose, have emptied themselves in the desert, and the runnels are now dry and worthless. To put it plainly, the warring Powers have, some entirely, others more or less partially, turned their attention from profitable production, the output of wealth, the exchange or use of which will produce new wealth, to the production of instruments of destruction. When these instruments are utilised they not only consume themselves and leave practically nothing remaining, but they carry out a work of destruction which entails the loss of other accumulations or possibilities of wealth. Nor is the consumption of the instruments and munitions of war the sole or chief material loss to the combatants. The men handling those weapons have to be trained and transported to the field of action, fed during the period of their service, tended when sick or wounded, and clothed and housed in some sort. All these operations consume a quantity of food, clothing, and other materials of various descriptions, and there is absolutely nothing tangible to show for this expenditure.

To take our own case, five million men trained to industry, helping to carry on the business and trade of this country, would consume almost as much food and clothing and other materials as the men in the field and on the sea, but as a return for that consumption there is more than corresponding production of useful commodities, machines, ships, and railway stock, which in turn assist in the work of developing the natural resources of the world, or of directly taking part in the work of further production. Thus the position is that for two years we have been consuming our wealth, and to that extent must remain the poorer and be short of many of the goods and services we used to consider necessaries of life, until we have, by renewed efforts and a return to the industries and commerce of peace, taken measures to restore those useful things which have been consumed.

When the war ends, it will be incumbent on us all to redouble our activities, increase the productivity of mill, factory, and field; for, so long as there is a deficiency in excess of what we were accustomed to, so long must some of us, and especially the poorer members of the community, feel the pinch occasioned by this devastating war.

But, it may be asked, how are we to increase our productivity? The war, in spite of the suffering and loss occasioned, has not been all loss. As a nation—nay, as an Empire—we have found ourselves; but this thought, if developed, would lead us into spheres foreign to the work of this Section. We have taken measures which must result in improving the physique of our race. Of the many thousands of men who have been trained to arms and submitted to discipline the great majority happily will return when peace is made. The self sacrifice practised by these men will act as a leaven among our population—it has already done so. We shall emerge from this war a better-disciplined, a more serious people, better equipped mentally and physically to cope with new conditions. We have learned what hitherto had only been suspected or at most known to a few, that we have not produced anything like our industrial maximum.

An insidious element of friction threatening to develop into class war has been sapping our energies. There have been faults on both sides, but daylight is being thrown over the situation, and the waste and loss of this friction has been laid bare. If we do not take to heart this great experience and alter our ways for the better then we deserve to go down as a nation; but I am persuaded that the lesson is being learned, that the picture now visible of industrial waste and loss—a loss that falls most hardly on the masses of the people—will not pass before our eyes unheeded.

Not only was there loss through friction between employers and employed, but in many industries we were continuing to use out-of-date tools and methods long after they should have been discarded. A long era of prosperity had not, indeed, caused decadence, but was threatening to do so. The war has shaken us up and shown us the realities of life, making the mistakes of the material side with which we have to do here plain and unmistakeable.

To beat the national enemy we had to re-equip our workshops, and the new equipment will be available to a great extent for future work. Moreover, we have been taught by a bitter lesson that up-to-date equipment is as necessary if we are to maintain our position as an industrial and commercial nation as it was to enable us to maintain our international position.

Friction between employers and workpeople led to restrictions on output, indifference led to utilising old tools and methods; both meant decrease of productivity. The necessary increase can be readily obtained by remodelling our system in these respects. How this can be carried out so far as reorganisation of the industrial forces of this country is concerned will be developed later, and is dealt with in greater detail in the Report presented by a Committee ot investigation which has been working for this Association.

Attempted Forecast of Our Industrial Future.

I want to attempt now to make a forecast of what may be expected in the commercial and industrial spheres when we sheathe the sword. Germany has overrun some important manufacturing districts. Belgium, North-Western France, and Poland have not only been occupied by the enemy, but machinery and industrial equipment have in many cases been removed to Germany. It is reported that railway tracks have been torn up in order that their materials might be used for military purposes elsewhere. The busy industrial areas mentioned have undoubtedly suffered very considerably, and will require to reconstruct and re-equip towns and factories, and to reorganise the labour-force. To set commerce and industry at work again on anything like the previous scale must be a work of some time. On the other hand, in spite of every effort, Germany has found it impossible to interfere with the industries of the United Kingdom either by force or intrigue; nor have the Entente Powers as yet invaded Germany. Indeed, for the purpose of this forecast it is wise to assume that German industrial equipment will not be affected detrimentally by the war. Even though we should invade Germany with a view to inflicting, not only defeat, but punishment, our purpose will not include industrial destruction. We shall undoubtedly do our utmost to punish those, whatever their rank, who have been responsible for the many crimes committed against humanity during the past two years. But this does not necessitate the ruthless destruction of mill, factory, or mine. We can quite adequately punish Germany without putting ourselves on a par with her in methods of destruction and brutality. The military caste must be summarily punished and the entire nation must be made to realise the sentiments of horror that their delight in the sinking of the *Lusitania*, the executions of Miss Cavell and Captain Fryatt, have aroused throughout the world. Every instance of insensate brutality must be atoned for by the guilty parties, and the nation as a whole must be taught such a lesson as shall make a repetition of those savage methods impossible. We feel our ability to carry through this salutary work, but when this is effected and when once again the world begins to get into its normal stride, so far as one can foresee, England and Germany will for some time be the only two European nations prepared to take any considerable part in international trade.

Meantime, during the period of the war, two countries —the United States of America and Japan—have enjoyed new and unlooked for trading advantages. So far as competition from the United States is concerned, it is probable that we need not feel unnecessarily pessimistic. The South American States are at the beginning of a period of development which may well prove to be rapid. The possibilities opened up by the Panama Canal route, even though the present canal should prove a failure, will not be resigned before another attempt is made to pierce the isthmus; that a cutting will eventually be made is, in my opinion, beyond question. America's developments, then, may be expected to take place principally on the American continent, in the Pacific, and in the Far East. In these regions there is ample room for both British and American enterprise.

Nor will Japan, for some time to come at any rate, compete with our staple manufactures.

The development made by Japan during the war would seem to indicate that it is Germany, and not Great Britain, that will have to bear the brunt of Japanese competition. Small goods and fancy articles which came freely into our markets from Germany and Austria before the war are now being made in Japan. Our merchants, being unable to get supplies of these goods, sent samples to Japan, with the most satisfactory results as to price, finish, and quality. Thus we have been able to extend our business relations with our Ally at the expense of our enemy. Moreover, although there is no certain information on the subject, it is more than possible that when normal trading is resumed it will be found that Japan has been extending her business in these and other classes of goods into other markets hitherto the preserve of the Central Powers.

Hence it is of special interest to attempt to forecast to what extent and with what prospects England and Germany will be in competition in international trade after the war. This will depend for the most part on two sets of factors:—(i.) The internal industrial condition of each country, and (ii.) commercial factors. So far as the former are concerned, there is much that this country should realise and take to heart.

The United Kingdom, in spite of the war and its heavy drain on our resources, has been enjoying an exceptional time of seeming prosperity. A large section of the workpeople have been earning high wages, whilst some employers have been earning handsome profits. High prices, high wages, high profits have been the order of the day. The return of peace will very considerably modify the last two of these, and how will those affected face the change?

To understand how the parties will answer this question, certain agreements must be remembered. Foremost among these is the State guarantee that certain Trade Union restrictions and Government regulations which have been in abeyance for the period of the war shall be reimposed when peace is restored. If we were reverting to pre-war conditions there would be much to be said for this, but one hopes that both parties realise fully that conditions have radically changed, and that in consequence both employers and workpeople must be prepared to meet the new situation in a new spirit. Why were these agreements and regulations set aside? Because it was known that they hampered output, and our military success depended upon our producing the greatest possible amount of munitions of war. Our commercial success will now equally depend on getting the utmost possible production out of our industrial equipment. Are we then going to restore these obstacles just at the most critical moment?

With the return to more normal times the national necessity for war stores and munitions will cease, and our industrial forces will have to rely on the home and foreign markets for employment. Foreign competition will almost certainly be greatly intensified. There may be at first a great demand for manufactured goods of all kinds, as a consequence of decreased supplies during the war, but all the principal trading nations will strain every nerve to get the greatest possible share of orders. If, under such circumstances, we indulge in an internal struggle between Capital and Labour, instead of bending our whole energies to retain and extend our hold on markets, we shall lose an opportunity which is not likely to return. And yet there is a widespread expectation among employers and workpeople that the European war will be succeedad by serious industrial strife.

So far as the commercial factors are concerned we have almost everything in our favour. We have not outraged the sentiments of humanity by employing inhuman methods in waging war. We have retained our position as the headquarters of the money market. We have our shipping resources and equipment practically intact. Our merchants and exporters are keen and ready to carry on their business with even greater energy than before the war. We have arrears to make up, but have the will, and, with harmony at home, the ability to carry on a more extended trade. Our capital has not been seriously affected, and there are no signs that it will be—our financial establishments and banks are prepared to do their share.

Turning to Germany, there is a most interesting condition of affairs to study. If beaten in the war Germany will be a poor country; the economic position will be deplorable, but hardly irreparable. Every section of the community has already felt to some degree the effects of the war. When peace comes there will be a determined attempt to regain the old position. A disciplined people, acting under a Government that will be compelled by circumstances to foster every possible means for repairing the broken machine of trade and for restoring the national wealth, will without any doubt be prepared to make heavy sacrifices to regain what has been lost. The Government will offer advantages in the shape of low railway rates and canal facilities, and, as far as possible, bounties on export business and on shipping to encourage and extend foreign trade. Manufacturers and merchants will cut down profits, and workpeople will be carefully taught that only by increased productivity and by a period of low wages can that which has been lost be regained. One foresees a remarkable attempt by a united and determined nation to make good in as short a period as possible a waste and loss occasioned by the war and the blockade. German goods for export will be cheap, and the low price will be still further emphasised by the depreciation of the mark. For so long as the mark is at a discount there will be a *pro tanto* advantage to export trade, and although the mark may eventually regain its par value, a few months or even weeks will have an appreciable influence on reopening foreign business.

Thus a comparison of English and German possibilities in foreign trade on the resumption of peace shows that there are certain advantages on both sides. The German advantages are solid and appreciable, but if England is seething with industrial friction the advantages she possesses will be neutralised and her failure a certainty.

This leads us to consider whether a policy can be devised which will remove causes of friction and assure to our industries a new era of prosperity.

The Need for National Organisation.

It is at first sight curious, but still very natural, that Press and public should from time to time be obsessed with one idea. As the war developed there has been a growing tendency to demand Organisation in every sphere of national life. The striking successes scored by Germany have been universally, and probably rightly, ascribed to thoroughness of organisation and complete preparedness before provoking the conflict. As a consequence, a comparison has been made between English and German military policy, greatly to the detriment of the former. And, not content with this, further comparisons have been made, with the result that, if one believed all that was printed in the newspapers or accepted what passes in private conversation, we should be led to believe that rule of thumb has been the leading British characteristic. It has been forgotten that Germany has for many decades prided herself on her Army, even as England has relied on her Navy. One has been a great military power; the other equally great at sea. The test of war has proved that Germany was a very difficult country to oppose by land, but that in naval matters England is supreme. The economist, however, has to go further and investigate into those matters which are connected with his science—namely, the production, the distribution, and the consumption of wealth. Can it be said that the want of organisation and other faults of our military system are typical of what has been going on in the industrial and commercial sphere? I for one cannot bring myself to accept the truth of this. Had our economic interests been carried on under so-called War Office principles we could not have built up the great position we occupy as world traders. What, then, are the facts? To answer this question one should remember the leading facts connected with our industrial development. This brings out some points which the superficial observer inevitably misses. For upwards of a century our industries have been gradually developing, and the progress has, on the whole, been along healthy lines—each decade has seen some advance more or less great.

German attention to industry and commerce is much more recent. She was able to benefit by our experience, nor was she slow in doing so. To take a simple illustration. A manufacturing firm of fifty years' standing has developed a system, and has equipped factory and workshop as occasion demanded. A rival, seeing the possibility of competing successfully in the same business, organises a new company, raises the necessary capital, and is able to commence operations with plant, machinery, and equipment of all kinds absolutely up to date, and even with some new improvements. In these circumstances, provided that the management be good and that there is a demand for the goods produced, the new firm has on the manufacturing side considerable advantages. The older firm, however, is not devoid of advantages. It has a certain connection, a goodwill, and with able management these will enable it to compete with the newcomer, whilst the managers will have time to consider how to put the manufacturing side of their business on a par with that of the rival firm. The position in a simple instance like this is fairly easy to understand. In the case of a nation, with its many and varied interests, it takes a very much longer time for the situation to develop. The agitation for Tariff Reform and Colonial Preferences is a proof that several years before the war broke out some Englishmen were awake to the fact that a new condition had come into existence, and that, if we were to preserve our advantageous position, we must take careful stock of newly-arisen factors in world-trade. For Germany was not the only one, nor perhaps the most serious, of these factors. The United States of America, from the time of the Civil War, had bent her energies to the work of internal development. Having concentrated on this for nearly forty years, she began to expand a world-policy both political and commercial. Japan, too, emerged with unexpected suddenness into the arena. Thus, as the nineteenth century drew to a close, the economic interest of England required careful and earnest attention. The fiscal controversy undoubtedly had the great and important effect of waking English traders out of the lotus eating condition into which they were in danger of sinking. All our principal and many of our less important industries were carefully reviewed, with results that can be realised by a study of the annual statistics published by the Board of Trade. There was, however, a very subtle policy being pursued, which required very minute knowledge and wide experience to grasp. It was our proud boast that we left trade free and untrammelled, that we believed in the health-giving effects of open competition. It needed the stern lesson of the war to make known how this generous policy could be utilised to our detriment by a rival commercial nation. The facts as to the exploiting of the mineral resources of the Empire, as to how the dye and colour industry and various by-product industries have been developed so that certain vital trades almost passed under foreign control, came to light only just in time.

It became plain, as these facts leaked out, that we needed a better system of industrial and commercial intelligence. There was also a lack of unity of working among our principal industries incompatible with the growing interdependence which had been a marked feature of modern economic life.

Hitherto, apparently, it has been no one's business to survey comprehensively the resources whence our raw materials are drawn. Even those resources within the Empire have been nervelessly left to be exploited by the first comer, and the mask of an English name has enabled foreign capital and energy to divert some of our valuable minerals to foreign countries, whence we have been compelled to purchase them at unnaturally enhanced prices. Sufficient of the facts have been made public to warrant the demand for reconstruction and improved organisation of those departments responsible for the national trade.

It would be most unwise as well as ungenerous to attempt to blame our Board of Trade. That department has, on the whole, worked hard and well for British interests. But it is both wise and necessary to criticise the policy that has overweighted this one Government department. And although there should be very careful consideration before either recommending or making a drastic change, attention ought to be given to the frequently expressed opinions of both Chambers of Commerce and individual traders in favour of the creation of a Ministry of Commerce. To this Ministry there might be transferred some of the functions of the Board of Trade, whilst at the same time the new Ministry might be responsible for maintaining that general survey over trade and commerce without which any organisation we may attempt would be incomplete.

If this view be accepted, it is not fair to charge our industrial interest with lack of organisation. An examination of any one of our industries—shipbuilding, shipping, the manufacture of various goods for export—shows that each have been well, and in many cases exceptionally well, organised, but the organisation requires to be completed by some machinery with responsible officials to co-ordinate the organisation of the several interests. Even in this direction something has been attempted. The Associated Chambers of Commerce gives, at any rate, the germ of an organisation for attending to this great need. We may ask whether this could be still further elaborated so as to give the country what is wanted. Have our Chambers of Commerce sufficient standing to make their association strong enough for the work, or should we look to the State to supply the keystone to the arch? The answer to this will depend on the views of the individual attempting to give it. Perhaps the time has come when a word of warning should be uttered. Are we not getting rather too prone to fall back upon the State? We were, and perhaps still are, the most self-dependent people in existence. Both the employer and the Trade Union have in the past been but little inclined to turn to the State. Can the completion of our industrial and commercial organisation be adequately attained by the interests concerned or must we look to another State department or sub-department to effect what is required? Our past history seems to suggest that before turning to the State we try the initiative of the interests at stake. This brings us to a further section of the subject.

Industrial Organisation.

The organisation that has grown up with the development of our industries includes two very important but unequally developed sets of organisation. The Industrial Army of Labour force of this country includes all those who either organise industry or take any part, however important or however humble, in its working. From the captain of industry, or *entrepreneur* as our brave Allies call him, down to the humblest weekly wage-earner, we have a labour force which ought to be looked upon as one and indivisible. In connection with this force we now have two sets of organisations whose interests some people consider to be antagonistic. I would emphasise the fact that these two are really one force, their main interests are identical, and they can best serve those interests by striving to minimise differences and by doing all that is possible to work in harmony.

Though theoretically one, the labour force has internally developed two sets of organisations. Manual labour has its Trade Unions; the organisers of industry have their Associations. British Trade Unions have a fairly long history behind them, and may be said to be in advance of any similar unions the world over. But the fact that of recent years there has been a tendency for small unofficial sections of given unions to kick over the traces and disregard the policy and agreements of their leaders shows that perfection of organisation has by no means been attained.

Employers' Associations are of more recent formation, nor have they so far attained to anything like the same completeness. Both organisations, especially the employers', are in need of further development. It is hardly for the economist to show how this can be effected. He can point to imperfections and make suggestions—only those conversant with practical working facts can formulate a practical policy. The most patent defects of these associations are due to the very virtues of their members. The individual British business man is unexcelled by the business man of any other country. In times of rapid transition and crisis he has again and again shown his leadership. He knows his business thoroughly, and as a working unit he has taken a very high place. But one of the most marked developments of modern trade is a growing interdependence of industries. Hand in hand with this we have become familiar with another phenomenon, the amalgamation of businesses of various dimensions into one great company or corporation. This phenomenon is common to both commercial and manufacturing interests. It is as marked among banks as among steel and iron companies. The comparatively small manufacturer or business man is giving place to bigger and inclusive organisations. These two and somewhat parallel developments are making a new demand on the individual. He and his predecessors exemplified individualism, the new stage upon which we have entered demands a modification of the old policy. Business, like everything else, is subject to evolution, and evolution on healthy lines can only be obtained by grasping fundamental facts and applying experience in accordance with economic laws. There need be nothing revolutionary about the required changes in our business organisation. We merely have to note what has already occurred, mark healthy tendencies, and clear away or prevent obstructions to natural growth. Our past history amply justifies us in pursuing this policy without uncertainty as to the result. Our entire industrial history is one of the best examples of steady and on the whole well-ordered evolution. We have shown our ability to adapt ourselves to the needs of the moment. As a race we are healthily conservative without being reactionary. That is to say, we know how to preserve what is good in the old and amalgamate it with the new. In other words, our organisation enjoys that useful quality of elasticity which enables us to keep abreast of the times.

Bearing this in mind, where are the defects of our business man, and to what does he need to give attention in order to come into line with the most recent requirements?

As I have just said, our business man's qualities emphasise his defects. For generations our business men have worked as units, and individualism has become almost second nature. The call now is that the individual shall sink a part of his personality and become, so far as one side of his activities is concerned, a member of an association. We have had Employers' Alliances, Federations, and Associations. Some have failed, some have managed to keep afloat, others have had a certain amount of success. None have hitherto quite attained to what is required. To the onlooker it would appear that when our employers meet as an association there is a lack of sympathy among the members, and if this should persist it would be fatal. Each individual knows his own business; he does not know, and perhaps it would be true to say he does not care to know, his neighbour's concerns. At any rate, as a result there is a lack of cohesion, there is a lack, too, of that co-operation which is required if the association is to be really successful and accomplish the objects for which it has been formed. This working in co-operation, the large organisations of capital, and the working together in associations, are comparatively new things to our business community. Time and experience will put things right; at present we have not accustomed ourselves to a newly developing condition of affairs. Our business men, then, need to focus their attention on these early ailments of the movement and get them removed as soon as possible.

A second group of defects arises indirectly but almost inevitably from that which has just been considered. Some alliances, rings, and associations have failed and come to an end. And in certain cases the cause has been unmistakeable, for there has been a lamentable want of loyalty, and even in some cases it must be said honesty, to the agreements entered into by the association.

Only to mention one group as an instance of this—the New Trades Combination Movement, which caused quite a considerable stir during the late 'nineties of last century, especially in the Midlands among the metal trades. Articles appeared in the journals, and a book ("The New Trades Combination Movement," E. J. Smith—Rivingtons, 1899) was written explaining the movement, and great hopes were entertained that a new era had opened out before both Capital and Labour. But all ended in a failure. There was for a time a kind of Syndicalism—a syndicated industry enabling employers to increase their profits and the workpeople to earn abnormally high wages. So long as competition could be kept out of the market things went swimmingly, and a specious prosperity developed. But the consumer was being exploited—the increased prices charged for such goods as metal bedsteads gave would be competitors and unscrupulous members of the alliance their chance. The cheap wooden bedstead, however, made its appearance on the one hand, and on the other there were such things as secret discounts and commissions, and this special alliance ended in failure. The history of that short but industrially instructive movement has yet to be written. Its cardinal facts should be known to those who now have an opportunity for shaping the industrial future of this country.

Three lessons stand out from this experience:—

(i). We must learn to work together in association.

(ii). All members of an association must be absolutely loyal and honest to their engagements, either written or implied.

(iii). Such associations must be regulated or the community will be exploited.

Nor is it impossible to suggest a method by means of which this may result. When Employers' Associations have justified themselves it should be possible to obtain State recognition for them, and it would be practical politics, when both Employers' Associations and Trade Unions have developed to the point at which both merit State recognition, to enforce under penalty agreements made between them on all those, either employers or workpeople, who wished to work at the industry within the area under the recognised organisations. Thus it would not be necessary to make membership compulsory; self-interest would be the extent of the pressure.

Turning to workpeople's unions we also find defects which require removing. The policy of union has been practised among the workers for upwards of a century, and for at least half that time with well-marked success in certain directions. In the first instance it was the aristocracy of labour that realised the advantage of collective action, but, notably since the late 'eighties of last century, efforts have been made to extend the policy to all grades of labour. Hence the ailments which have to be noted are rather more mature than those affecting Employers' Associations. Success in certain directions has perhaps led some of the more ardent spirits to expect more from their unions than working conditions allow. The experience of old and tried leaders has led them to adopt a more cautious policy than the young bloods are inclined to accept. Hence there has been a want of loyalty, different, it is true, from that met with among employers, but equally disastrous if persisted in to the object in view.

All the men in a given industry should be members of the union, provided that the union is well organised and ably administered. This should, however, be the result of self-interest and a regard for the good of fellow-workers, rather than of compulsion; how that may be attained has been suggested. Perfection of organisation will come when workpeople not only realise the real possibilities of collective action, but are prepared to follow loyally leaders who have been constitutionally elected. The leaders are in a better position to know the facts of the case immediately under review, but if their leadership has been found faulty there should be adequate machinery for replacing them with men who command the confidence of the majority of the members. When agreements have been entered into the terms should be implicitly observed, even though they may turn out to be less advantageous than was expected. Periodical revision would make it possible to rectify mistakes or misapprehensions. But it cannot be too strongly emphasised that for both sets of organisations the great factor making for smooth and satisfactory working is absolute loyalty to the pledged word. A large employer of skilled labour writing to me on this point said:—"In my opinion no industrial harmony can exist between employers and employees until Trade Unions through their Executives can compel their members to adhere to and honourably carry out all agreements entered into with the employers. . . . In fact, until a more honest code of morals exists on both sides no improvement can be looked for."

Further, there is a need for a more complete and authoritative central authority, both for individual industries and for federated trades. The machinery for this exists; it merely requires development. When the local and central machinery has been perfected, the right to *strike*, which, in common with the right to *lock out* as a final resource, should be jealously maintained, would be carefully regulated, and would only be resorted to as the considered judgment of the most experienced men on either side. It should be impossible for either an individual association or a section of it to order a strike or a lock-out on its own responsibility.

What, then, do I consider should be the main outline of industrial organisation? Employers should be organised into:—

(*a*) Associations of one trade in a given district.
(*b*) National Associations of one trade.
(*c*) Local Federations of trades.
(*d*) National Federations of trades.

Of these, (*b*) and (*d*) should be organised under a system of representation.

Workpeople should have unions and federations corresponding to those of the employers, and in both cases the National Federations should be carefully organised Councils who would enjoy a large measure of authority, tempered by the necessity to win and preserve the confidence of their electors. From these two representative bodies there could be elected an Industrial Council as a Court of Appeal, representative of the whole industrial activity of the country, and so far as these various bodies were approved by the State they would enjoy far-reaching powers.

Approval by the State should depend on the observance of moderation and working in conformity with carefully devised regulations. For the State in this matter would be the representative of the consumer and of the national interest. Without this you get something not very far removed from Syndicalism, but under careful regulation abuses might be avoided.

At the head of the organisation there would be a real

Industrial Council representing the industry of the country. The Industrial Council established in the year 1911 has never had a fair chance to show its mettle. It was established at a critical time; perhaps the Government did not feel justified to throw a great responsibility on an untried body. Nevertheless it exemplified a very wise policy, and one regrets that it has not been tested, for even now both employers and workpeople feel that some such Council is preferable to State interference, and there is a clearly articulated distrust on both sides of official arbitration.

We do not need at the present juncture to attempt a new experiment. Our old system, whatever its failings, have been tried and proved sound. Its elasticity has been its salvation, and it is capable of still further evolution without calling for drastic changes. The improved organisation that is now suggested would contain nothing that is new or untried. It would consist of natural developments of what already exists. Employers and workpeople have organised themselves into associations and unions, some of these have developed federations of similar or even of unconnected interests, and both parties have their national congresses, or at any rate the germ of them. The demand now is that the organisations already in existence be perfected, and that those perfected organisations shall in all their agreements be loyally and honestly supported by their members. Success depends on absolute loyalty to the pledged word.

Here we have a practical policy suited to the needs of this critical stage in our history. The ideal organisation has yet to be formulated, but what is here proposed would form a definite step in advance, and the very elasticity of the system would be a good augury for the future.

Among the innovations recently introduced into this country, and one calculated to have important effects on our industrial well-being, is automatic and semi-automatic machinery. We have been accustomed to the use of labour-saving machines—indeed, this country was the birthplace of many of them. The re-equipment, however, of our factories for war purposes, both in tools and workpeople, has wrought a revolution comparable with that effected by the introduction of the steam-engine.

From the point of view of craftsmanship our old system had much in its favour. Our mechanics in certain trades had to be highly skilled, for the description of work turned out made considerable demands on the operative. In America and Germany standardisation has been carried very much further than in this country, and consequently repetition work was much more generally practised than with us.

One may grieve over the passing of our old methods, as one is sometimes tempted to regret the days of cottage industries. Neither, however, is compatible with modern conditions, and an important part of the work of reconstruction and reorganisation will be connected with standardisation and the further introduction of repetition work. This will call for the exercise of careful and experienced industrial statesmanship if trouble is to be avoided, for agreements will have to be framed which will in the long run work equitably and satisfactorily to all the parties concerned.

A Committee of this Association has been investigating for the past two years into the extent to which women have recently replaced men in industry. A certain amount of exaggeration exists as to the number of women who have entered our factories or undertaken services left vacant by men who have joined the Forces. The total number is in round figures about 600,000, as against five million men who have joined either the Navy or the Army as a consequence of the war.

The entry of large numbers of women into industry has been viewed with a certain amount of alarm by the men; and Trade Unions have naturally stipulated, where possible, that these women shall receive the same rates of pay for the same work as the men, and that when the men return the women shall give place to them.

That there was little ground for alarm as to the influx of women can be realised by a consideration of a few facts and figures. The majority of men who enlisted were workpeople of one sort or another; of these, unhappily, some have been killed in battle or have been rendered incapable for work. Even so, the majority will come home requiring occupation. What opportunities will they find?

To answer this question at all satisfactorily it is necessary to consider some determining factors. Thousands of men have left indoor occupations and their accustomed town life and have been trained, drilled, and disciplined under open-air conditions. They have lived, worked, and fought in the open country in some cases for many months. The new experience has had potent effects. Physique has improved, the outlook on life has changed, in many cases new hopes for the future have been formed. Inquiry shows that there is a division of opinion as to the extent to which disbanded members of the Forces will decide on making a radical change in their mode of life. Yet the experience of what occurred after the South African War warrants us in assuming that considerable numbers will only return to indoor occupations and town life if there be no alternative. It is too soon yet to form an opinion as to what opportunities there will be for land settlement. But it is known that offers will be made both at home and in various parts of the Empire. A moderate estimate of those accepting these offers, and of our losses of killed and permanently disabled, would be at least one million. Then we shall undoubtedly require, at any rate for some years, a much larger standing Army. Even on a peace footing this at a moderate computation may be put at a million men. These two figures, and neither of them err on the side of exaggeration, will absorb two million men who will be permanently lost to the old occupations.

Moreover, there is good ground for anticipating that if the war concludes before our resources are unduly strained, and there is every prospect that it will, there will be a period of good trade. We have to restore our own depleted stocks of goods, our mercantile marine demands a large amount of new tonnage, railways and other transport services will require much new equipment. Turning to the Continent, parts of France, Belgium, and other of the Entente countries will need reconstruction works of considerable proportions, and in this work we shall play a great part. World markets, too, have been kept short of many manufactured goods. We shall be in a position both to finance and carry on a greatly extended system of industry and commerce, for not only is our banking system prepared to face this, but our man force has been greatly improved, and our industrial equipment to a great extent remodelled.

Reverting to the somewhat thorny question of the women who have been engaged on what were men's occupations, I see no cause for alarm. Many women came forward from motives of patriotism and will gladly resume their former state. The question, I believe, will rather be how can we obtain the labour necessary to cope with the post-war demand.

The new equipment of our factories will place us in a position to increase very greatly our output, and this should enable us not only to face a possible labour shortage, but if the recommendations made by this Section of the Association meet with a favourable response, our labour force should enter upon a new period of prosperity consequent on a remodelling which has been rendered possible by a reorganisation of our industrial machinery. This new epoch for labour would include higher wages, shorter hours, and better working conditions. To effect these salutary advances both employers and employed need to exercise sanity of judgment, frankness in mutual discussions, and a recognition of the fact that the prosperity and material well-being of each is bound up in a common effort to maintain and develop our industrial and commercial position.

REFINING VEGETABLE AND ANIMAL OILS.*

By CHARLES BASKERVILLE, Ph.D., F.C.S.,
Professor of Chemistry and Director of the Laboratory, College of the City of New York, Member of the Institute.

(Concluded from p. 174).

Some four general methods for refining oils have been and are being worked in practice. They are:

1. Treatment with steam (plain or superheated) whereby some coagulation results and many odiferous substances are driven off. This does not diminish the free fatty acid content of the oil so treated.

2. Treatment with variable amounts of concentrated sulphuric acid (Gower, 1792) under determined conditions of heat and agitation with or without air. The oil contains certain substances which, when flocculated by the acid and temperature, fall down and mechanically (a term used in several recognised authoritative books) carry down other impurities. This process does not diminish the acid content of the oil so treated.

3. Heating up under carefully-regulated temperature conditions with fullers' earth, bone-black, &c., and filtering. This process also yields an acid oil.

4. Adding caustic alkalis, or alkaline earths, of an amount and strength determined by laboratory experience (Barreswil, beginning nineteenth century), heating to the "break," settling and drawing off the oil, which floats upon the soap stock or "foots." This was supposed to give a neutral oil, but not until it had been washed several times with water.

Yet as late as last year a distinguished oil chemist, in a very interesting summary of the "Contributions of the Chemist to the Cotton-seed Oil Industry" (*Journ. Ind. and Eng. Chem.*, 1915, vii., 277), said "the chemist . . . found that the quality of the oil followed the free fatty acid present." An empirical formula has been worked out to show this relationship to the free fatty acid. The rule is: Multiply the f.f.a. by 2 and add 4: that is, an oil showing 2 per cent f.f.a. should give a shrinkage of 8 per cent. This is true only in a general way. I recently had a cotton-seed oil with 1·7 per cent f.f.a., which showed a shrinkage of 21 per cent by the official method of the Cotton-seed Crushers' Association.

The writer quoted above further said "the chemist's greatest service to the industry has been in the refining of the oil . . ."

Wesson was here referring more especially to edible cotton-seed oil. In that connection, Lewkowitsch, the lamented Anglo-German specialist in oil chemistry and technology, has said: (Vol. ii., p. 32, 3rd Edition) "No chemically-treated oil or fat can be looked upon as a product fit for human consumption." I confess inability to comprehend this sharp distinction as to what is meant by a "chemical." Oxygen from a chromate is a chemical; oxygen of the air is not. Sulphuric acid is a chemical; caustic soda is not. It may be interjected here that certain statements transmitted by texts and sanctioned by law call for clarification and revision. No treatment of an oil or fat, which involves purification, rendering it palatable, agreeable to the sight, and avoids the introduction of constitents which may interfere with normal digestion should be forbidden. For fear of misunderstanding, it may be stated here that the method described below complies with all the most rigid laws of all nations and even the abovementioned uneven discriminations.

An oil that is acid is unsatisfactory as a food. Acid oils corrode the vessels and generate objectionable gaseous products when used as burning fluids. Acid oils corrode the bearings when used as lubricants; so it is desirable to have neutral oils for many purposes. Yet a neutral oil does not "cut" into white-lead, for example, so an acid oil is preferred as a paint-vehicle; but Gardner has pointed out that the oil should not be too acid.

I have been more concerned with neutral oils and their production, so shall confine my remarks to preparation of that class of substances.

The present customary practice for refining vegetable oils referred to (the fourth mentioned above) depends upon neutralising the free fatty acids in the crude oil usually by agitating the oil with an aqueous solution of an alkali, the strength and the amount having been previously determined by laboratory tests, agreed upon as a standard, and then heating the mixture during agitation to a suitable temperature until the oil "breaks." The mass is then allowed to stand until the "foots" settle to the bottom of the kettle, when the supernatant oil is drawn off by means of a swivel syphon. According to the process of Chisholm sodium silicate is added to facilitate the settling. Invariably some "dreg" floats on top of the oil. If this be very great its settling is sometimes facilitated by throwing salt on top of the oil in the kettle. The salt drags down some of the floating "dreg." In any event the oil drawn off is clouded, perhaps on account of the presence of some dissolved soap or globulated moisture or suspended matter—all doubtless colloidal in nature. This oil is then "brightened" after drawing off by throwing in small amounts of fullers' earth, beating again, and passing through a filter-press. Sometimes, previous to this treatment with fullers' earth, the decanted oil is heated to 160 to 180° F. in a settling tank to cause the "foots" remaining in the oil to rise to the top, when it is skimmed off.

The time factor in settling (six to twelve hours) of the "foots" materially affects the completeness of the separation referred to above. Cocoanut oil sometimes requires forty-eight hours to settle. In any event the "foots" is wet with oil. The "foots" also entrains oil. Consequently during the rush season the efficiency of yield of refined oil must be sacrificed for speed and quantity refined. In other words, the more speed in refining the more loss of refined oil, whatever the analysis, upon which purchase and sale are based, may indicate.

A process which would reduce the amount of oil entrained in the "foots" to a minimum, thus increasing the yield of refined oil, and one which would not be dependent upon the slow subsidence of the "foots" (that is, admit of rapid separation with consequent increase in capacity of a refinery), therefore, seemed to me not only to be desirable, but if secured would approximate the highest efficiency one might hope for in such an industrial operation.

I have succeeded in working out such a process, and shall now proceed to describe the principles involved and at the same time demonstrate it to you as an analytical method. I have pleasure in exhibiting to you samples of the crude and refined (by my method) oils from a variety of sources.

The technical laboratory tests with batches of twelve to twenty lbs. have been verified in the factory on a commercial scale. Some of the samples exhibited are from factory runs.

The aims to be accomplished are:—

1. To reduce the amount of oil entrained in the "foots," thus increasing the yield of "whole oil."

2. To reduce the time of contact of the excess alkali (necessary for the "break" and to secure the best colour) to the minimum.

3. A technological corollary calls for the utilisation of any by-products.

It is to be assumed that all oils, good, bad, and indifferent, are to be treated. However, this may not be necessary, as in some cases only the good and perhaps the indifferent oils are refined under the old practice at some places. Certain foreign markets call for a highly coloured oil, so they do not present the problem of bleaching.

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* From the *Journal of the Franklin Institute*, June, 1916. Presented at a meeting of the Section of Physics and Chemistry, held February 10, 1916.

In my investigations, lasting through several years, I have taken various kinds of crude vegetable oils from various kinds of sources with various (extreme) conditions and refined them. In many cases I have been told that no attempt would ordinarily be made to refine a particular oil, as it should be sent to the soap-kettle, the corresponding price only being expected. Such oils would have represented much better values if they could have been refined by the usual practice. These oils in every case have yielded to my process, have been refined, and with a saving over the old processes. I may say, however, that China wood (tung) oil, castor oil, and aged linseed oil cannot be economically refined by the process. I wish also to repeat that I am referring to the production of neutral refined oils only.

If we can get the "foots" into such a condition that it may be filtered and then squeezed we may reduce the amount of "whole oil" entrained.

If we can do this immediately after the "break" and while the oil is still hot we shall be able to reduce the time the "whole oil" is exposed to the saponifying action of the excess alkali necessary to secure proper colour, avoid the present practice of necessary "cleaning," and the second heating,

I have called your attention to the presence of bodies, which in general terms are called colloids, in oils. These colloids may or may not be coloured, may or may not make the oil turbid. I have also shown that some colloids may be and are coagulated by heat, some by acids, some by alkalis, some by salts or electrolytes, and in time will settle out. Colloids that have been coagulated or lumped may be filtered out. Some coagulated colloids in their formation adsorb colouring matter. The problem of economical filtration on the large scale necessary was one of great difficulty; in fact, so far as I am aware, it was unsolved previous to my investigation. Suitably prepared cellulose fibre will adsorb some colouring matter. It will bring about an agglomeration of the material precipitated from oils by treating the oil with alkalis and heating, and it will bind the particles together so that they may lose their somewhat slimy character and then may be easily filtered away from the oil in which they were produced. Short-fibred linters or "delint" is a suitable form of cellulose for some oils.

Therefore I add cellulose, suitably prepared, along with the caustic to the oil to be refined. The "break" takes place normally on heating, as in the ordinary process, but the precipitated mass is in such a physical condition that it may be separated from the oil immediately by filtration.

As mentioned above, some colloids, perhaps coloured, are thrown down by salts, so in certain cases some salt (1 per cent of sodium chloride) may be added. If there be a slight excess of water present the sodium chloride serves also to "salt out" any soap in that water. The addition of salt, however, is not necessary in all cases.

I have also discovered that the tendency of the soaps formed by the caustic-alkali treatment to emulsify with the oil, or so to distribute themselves through the oil as to render their separation difficult, may be overcome by subjecting the oil at a suitable stage of the treatment to the action of an anhydrous salt which is capable of taking up water of crystallisation, the preferred salt being dry sodium carbonate (soda-ash), which, as is well known, is capable of taking up one, seven, or ten molecules of water of crystallisation, according to temperature conditions. By such treatment the soaps which have already been formed by the treatment with caustic alkali, and which have become so incorporated with the oil as to be incapable of complete separation by ordinary filtration, are hardened or pectised, presumably by dehydration, and are so modified that they are readily separated by simple filtration. Sodium sulphate, which acts in the same way, may be used instead of soda-ash.

The process is carried out by adding ordinarily 2 per cent of prepared cellulose (less than 1 per cent real cellulose) and a suitable amount of caustic soda (usually much stronger but actually less in amount than is commonly used). The whole is thoroughly basted by mechanical means and then heated to 45 to 65° C. to produce the "break;" a determined amount of soda-ash is added, after which it is filtered. At first some soap may pass through the filter-cloths. In that event the first filtered oil may be run directly back into the refining kettle and pumped through the press until the oil is "bright." This usually occurs within a few minutes; in fact the speed of filtration is directly dependent upon the speed of the pumps. This refiltration also improves the colour. This oil is neutral and can be deodorised and bleached, or both at once, or may be stored safely. If linters is used, one-quarter to one-half per cent of the dry cellulose is added.

These ideas are covered by four United States patents granted, Nos. 1,105,743, 1,105,744, 1,114,095, 1,130,698, and others applied for.

The danger of making a whole kettle into soap stock through failure of the refiner to be "on the job" is reduced to a minimum, as in several thousand trials this has not occurred, the trials being made by different people with various grades of oils of different character. In other words, the process is near "fool-proof." Any man of fair intelligence can operate the process, and the air of mystery surrounding the professional refiner is dissipated. The superintendent has a double check on the refinery by weighing the finished oil and cake. The daily reports when summed up should coincide with the annual inventory. I have known of cases where as much as 100,000 lbs. of oil have failed to appear in the annual inventory, but were reported daily, and had to be charged up to profit and loss at the end of the fiscal year when the operation was under the usual process.

Curves have been prepared from a series of cotton-seed oils very variable in character, and the comparative losses with several other oils by the normal present practice and my process.

I have also been able secure a further 1 to 3 per cent saving by subjecting the "cake" to hydraulic pressure.

The process is very rapid, the controlling factor being filter-press capacity. A study of plate filter-presses has indicated a preference for a centre-feed press making 1½ to 2-inch cakes. The filter-press problem in connection with the process is not one of filtering area but cake capacity. Presses, as the Kelly or Sweetland, which are dumped mechanically, meet the conditions better than plate presses. A new Sweetland press recently devised for this process promises the best results. It is provided with bottom exits for the refined oil, and the under bivalve swings through an arc of 165°. Monel metal filter-cloth makes the machine practically permanent. By a slight increase in filter-press capacity the output of a refinery may be doubled or even tripled.

Utilisation of By-product.

The cake may be converted directly into soap, the cellulose becoming very finely comminuted. It is partially mercerised, partly converted into a colloid, and some of it forms an unobjectionable filler for some grades of soap, especially soap powders.

The cake may be "cut" with acid directly. The cellulose settles quickly in the aqueous layer from the black grease, which latter may be drawn off ready for market or use. When the cake is to be "cut," in order to reduce the amount of acid necessary, I prefer to use salt cake in place of soda-ash as the "agglomerator."

A solution of nitre cake, the process of Dr. Jeffrey Stewart, of Philadelphia, patent assigned to the DuPont de Nemours Company, for the recovery of oil from soap stock, can also be used in cutting the cake. In view of the high price of acid at present this may serve as an economical method for making "black grease."

Printed instructions for the use of the method in practice or as analytical procedure will be supplied to anyone who will write for them.

Summary.

A process has been worked out, based on scientific principles, for preparing neutral oils, which possess the following advantages :—

1. The actual refined oil obtained is from 1 to 10 per cent more than now secured. Placed at a low average of 3 per cent, the process will save the cotton-seed oil industry in this country over 2,000,000 dols. a year when prices are normal. The soja-bean oil industry, just developing in this country, can save 5 per cent. The peanut oil industry can save 6 per cent. The cocoanut oil industry can save from 3 to 5 per cent.
2. The process takes from one-tenth to one-third the time now necessary. Hence the capacity of the refinery is increased. This is of great importance during the rush season; in fact its introduction will in economic efficiency perform the same *role* the tungsten filament lamp has played in the electric lighting industry, whereby the light production of a power station has been tripled.
3. The process gives a daily double check on the efficiency of the refinery.
4. The process is applicable to all grades of edible oils, which is not true with the common procedure.
5. Little new machinery is needed. The extra filter-press capacity called for will be more than paid for in the first year's profit.
6. The cost of chemicals is the same or less.
7. The by-product cake may be converted directly into a useful and commercial material.

ON THE VOLUMETRIC DETERMINATION OF TIN BY POTASSIUM IODATE.

By GEORGE S. JAMIESON.

The iodine and ferric chloride methods are the ones most commonly employed for the volumetric estimation of tin. The iodine method is based upon the titration of stannous chloride in hydrochloric acid solution with iodine, using starch as indicator, while the ferric chloride method in general use is based upon adding an excess of ferric chloride to a hydrochloric acid solution of stannous chloride, and titrating the resultant ferrous chloride with potassium permanganate. The iodine method has by far the widest application, as it can be used to titrate stannous chloride in the presence of ferrous salts as well as metallic antimony, which would react readily with ferric chloride.

The iodate method has the advantage over both of these methods in that the end-point is exceedingly sharp. Furthermore, there is far less danger of over-titrating the solutions. Another advantage is that extreme precautions to prevent outside oxidation of the tin during the titration are not necessary because the potassium iodate may be added very rapidly to the appearance of iodine in the solution, then without further precaution the titration can be completed as slowly as desired. It should be observed that the iodate method cannot be employed to titrate tin or stannous chloride in the presence of cuprous, ferrous, antimonious salts, or precipitated metals. However, in the majority of cases, it is a simple matter to avoid or eliminate these interfering substances and apply the method with satisfactory results.

The method to be described is based upon the titration of precipitated tin or stannous chloride with potassium iodate in the presence of strong hydrochloric acid, according to the general method of L. W. Andrews which has not been previously applied to the estimation of tin (*Journ. Am. Chem. Soc.*, 1903, xxv., 675). In order to test the method, a solution containing 3·567 grms. of normal potassium iodate in 1000 cc. was prepared. According to the equations of the reactions,—

$$KIO_3 + Sn + 6HCl = SnCl_4 + KCl + ICl + 3H_2O,$$
$$KIO_3 + 2SnCl_2 + 6HCl = 2SnCl_4 + KCl + ICl + 3H_2O,$$

the equivalents of this solution are respectively 1 cc. = 0·001983 grm. Sn and 0·003966 grm. Sn. The titrations were carried out in 250 cc. glass stoppered bottles in the presence of a cooled mixture of 30 cc. concentrated hydrochloric acid, 20 cc. of water, and 6 cc. of chloroform. During the first part of the titration, the potassium iodate was added rapidly while shaking the bottle so as to give the contents a gentle circular motion until the iodine colour, which gradually appeared, had increased to the maximum amount, then the stopper was inserted, and the solution was thoroughly shaken. The titration was continued with thorough shaking of the closed bottle after each addition of potassium iodate until the end-point (the disappearance of the violet colour of the chloroform) was obtained.

The first experiments were made using a solution of stannous chloride which was prepared by diluting 50 cc. of the laboratory reagent to a litre. The solution contained 225 cc. of 1 : 1 hydrochloric acid per litre, which was sufficient to maintain a perfectly clear solution. This solution was standardised by the iodine method on three different days as indicated in Table I. No precautions were taken to prevent the oxidation of the stannous chloride solution, and it was observed that the more solution removed from the litre flask the faster the stannous chloride was oxidised by the oxygen of the air admitted to the flask, as would naturally be expected.

TABLE I.—*Titration of Stannous Chloride Solution.*

Expt. No.	Date, May.	$SnCl_2$ solution. Cc.	KIO_3 used. Cc.	Sn (as $SnCl_2$) present. Iodine method.	Iodate method.	Error Grm.
1.	14	10·0	16·0	0·0636	0·0635	−0·0001
2.	17	10·0	14·9	0·0595	0·0591	−0·0004
3.	17	10·0	15·0	0·0595	0·0595	—
4.	18	10·0	14·8	0·0587	0·0587	—

From these experiments it will be seen that the iodate titrations checked the iodine titrations closely. The iodate method will be found very convenient to determine the amount of stannous chloride present in solutions. In cases where it is necessary to titrate considerable amounts of stannous chloride, it is recommended that a much stronger solution of potassium iodate be employed, as it is very important to have the solution at the end of the titration contain at least 10 per cent of actual hydrochloric acid to prevent the hydrolysis of the iodine monochloride.

For the next series of experiments a standard solution was prepared by dissolving exactly 3 grms. of pure tin in about 150 cc. of concentrated hydrochloric acid, with enough nitric acid to oxidise the tin to stannic chloride. Three grms. of tartaric acid were added, and the solution was diluted to 1 litre. Measured portions of this solution were placed in the titration bottles, in each of which was placed 2 grms. of high-grade 30 mesh zinc. After the reaction had proceeded for twenty minutes or longer, 40 cc. of 1 : 2 hydrochloric acid were added. As soon as the zinc had completely dissolved, leaving metallic tin, several cc. of potassium iodate were added, followed by 10 cc. of concentrated hydrochloric acid and a piece of platinum-foil to facilitate the solution of the tin. The titration was continued with very thorough shaking until the tin was practically all dissolved. Then 6 cc. of chloroform were added, and the titration finished in the usual manner. It is very important during the titration to add sufficient potassium iodate so that there is free iodine or iodine monochloride present in the solution at all times, otherwise some of the tin might dissolve, forming stannous chloride and hydrogen, and thus cause a serious error. A blank determination using 2 grms. of zinc and the same amount of hydrochloric acid as in the actual titrations required 0·40 cc. of potassium iodate solution, which has been detected from the amounts of solution (KIO_3 used), given in Table II.

Table II.—*Reduction by Zinc and Titration of Tin by Iodate.*

Expt. No.	KIO_3 used. Cc.	Tin present. Grm.	Tin found. Grm.	Error. Grm.
1.	15·0	0·0300	0·0297	− 0·0003
2.	30·4	0·0600	0·0601	+ 0·0001
3.	7·6	0·0150	0·0151	+ 0·0001
4.	30·2	0·0600	0·0599	− 0·0001
5.	24·0	0·0476	0·0478	+ 0·0002
6.	20·95	0·0420	0·0416	− 0·0004
7.	45·4	0·0900	0·0902	+ 0·0002

These results show excellent agreement with the amounts present, thus confirming the equation given in the first part of this paper. The solution of tin even in the presence of platinum was slow, and it was found that a titration required from half to three-quarters of an hour for completion.

An attempt was made to reduce stannic solutions to the stannous condition with nickel powder, which was made by reducing the oxide with hydrogen at a red heat. The nickel powder was found so reactive that unless large amounts were used, it dissolved so quickly that only a partial reduction of the tin was obtained. Since it appeared that nickel would be the most suitable reducing agent for general use with the iodate method, the next series of experiments was made using strips (1×5·5×0·1 cm.) of sheet nickel for the reduction, which was found satisfactory. The reduction was made in 250 cc. Erlenmeyer flasks provided with a 2-hole rubber stopper which carried a glass tube extending to within 1 cm. of the surface of the liquid. The other hole was provided with a short tube which extended a short distance below the stopper. Several experiments were made using measured portions of the stannic chloride solution described above. To each portion of this solution 15 cc. of concentrated hydrochloric acid and two nickel strips were added. The stopper was inserted, and the flask was heated on the steam-bath for forty-five minutes to ensure the complete reduction of the tin. Then a current of carbon dioxide gas was passed through the longer tube, and the flask was placed in ice-water. When the solution had reached approximately the temperature of the bath it was filtered by suction into a titration bottle (containing 6 cc. of chloroform) to remove the finely-divided nickel which had separated from the edge of the strips. The filter used was a calcium chloride prolong tube (10×1·8 cm.), provided with a perforated platinum disk upon which was placed a thin layer of absorbent cotton, a layer (2·5 cm.) of purified sea-sand, and another thin layer of cotton on top. Other filter mediums were tried, but were not found satisfactory. Before pouring the solution into the filter, a moderate stream of carbon dioxide gas was led in by means of a bent glass tube which extended to within 1 cm. of the filter-bed for a minute after starting the suction. The flask and filter were washed with small amounts of 1 : 1 hydrochloric acid, and the solution was titrated at once as described above. It was found necessary to make blank determinations under the very same conditions as in the actual experiments with each new lot of sheet nickel, and apply the corrections (due to the iron content of the nickel) to the subsequent titrations. The results in Table III. include this correction, amounting to 0·5 cc. of the potassium iodate solution. Several blank determinatinns were made upon the nickel used in this investigation with concordant results.

In order to apply this method to the determination of tin in solder and type metals, a sample of 0·2—0·5 grm., depending upon tin content, was heated in a 250 cc. Erlenmeyer flask with 15 cc. of concentrated sulphuric acid. It is very important to boil the solution gently until all the sulphur dioxide is expelled, otherwise it would be titrated along with the tin (*Am. Journ. Sci.*, 1914, xxxviii., 166). After cooling, 20 cc. of water and 15 cc. of concentrated hydrochloric acid were added, after which the tin was reduced and titrated as described above. The results are shown in Table IV.

Table III.—*Reduction by Sheet Nickel and Titration of Stannous Salt.*

Expt. No.	$SnCl_4$ taken. Cc.	KIO_3 used. Cc.	Tin present. Grm.	Tin found. Grm.	Error. Grm.
1.	30·0	22·77	0·0900	0·0900	—
2.	21·0	15·80	0·0630	0·0627	−0·0003
3.	18·0	13·60	0·0540	0·0539	−0·0001
4.	10·0	7·55	0·0300	0·0299	−0·0001
5.	9·9	7·40	0·0297	0·0294	−0·0003
6.	10·0	7·50	0·0300	0·0298	−0·0002
7.	10·0	7·50	0·0390	0·0298	−0·0602

Table IV.—*Analysis of Tin Alloys.*

Expt. No.	Name.	Alloy. Grm.	KIO_3 used. Cc.	Grav. det. Per cent.	Tin found Per cent.
1.	Type metal	0·5000	6·30	5·04	4·99
2.	Type metal	0·5000	6·25	5·04	4·96
3.	Type metal	0·5000	3·90	3·20	3·09
4.	Type metal	0·5000	4·00	3·20	3·17
5.	Solder ..	0·2000	19·60	38·76 (*a*)	38·86

(*a*) Iodine method.

It is recommended that an iodate solution containing 8·994 grms. of KIO_3 per litre (1 cc. = 0·01000 grm. Sn) should be used for the analysis of solders, using 0·5 grm. sample.

It should be observed in the analysis of type metals, &c., that when the filter becomes clogged with precipitated antimony, it should be heated with warm nitric and tartaric acids, and washed thoroughly with water and hydrochloric acid until all of the antimony is removed. Also it is advisable to keep the nickel strips free from deposited metals by frequent cleaning.

Since bronze contains so much copper it was found best to decompose them in the usual manner with nitric acid, and filter the metastannic acid in a Gooch crucible. After washing the precipitate it was transferred along with the asbestos mat to a 250 cc. Erlenmeyer flask, any metastannic acid adhering to the sides of the crucible being wiped off with a pinch of slightly damped asbestos and added to the main precipitate. About 15 cc. of concentrated sulphuric acid were added, and the flask was heated until the acid had boiled gently for two or three minutes. After cooling thoroughly 20 cc. of water and 15 cc. of concentrated hydrochloric acid were added. The asbestos was filtered off on a Gooch crucible, and washed with 1 : 1 hydrochloric acid, using as little as possible. Then the solution was reduced with nickel and titrated in the usual manner.

Table V.—*Analysis of Bronze.*

Alloy. Grm.	KIO_3 used. Cc.	Tin by grav. det. Per cent.	Tin found. Per cent.
0·5000	10·95	8·75	8·68
0·5000	10·93	8·75	8·66
0·5000	11·05	8·75	8·76

The results of this investigation show that tin may be estimated with accuracy by the iodate method, and that it is applicable to the analysis of alloys as well as solutions. With this titration it is important to maintain an acidity of at least 10—12 per cent of actual hydrochloric acid in order to obtain the correct reaction. Furthermore, it should be remembered that cuprous, ferrous, and antimonious salts, as well as any precipitated metal, will react with potassium iodate.—*Journal of Industrial and Engineering Chemistry*, viii., No. 6.

THE POISONOUS PRINCIPLE OF POISON OAK (*RHUS DIVERSILOBA*, T. and G.).

By JAMES B. McNAIR.

Botanical Similarity between Poison Oak (Rhus diversiloba) *and Poison Ivy* (Rhus toxicodendron). — The difference between *Rhus diversiloba* and *Rhus toxicodendron* is so small that their proper classification forms a bone of contention between botanists. Those botanists that believe in innumerable species are in favour of their separation, while the more conservative are opposed to it. Greene ("Leaflets of Botanical Observation and Criticism," 1903-1906, i., 119), considers *Rhus diversiloba* "a peculiar type of *toxicodendron* belonging exclusively to the Pacific coast." Engler believes *diversiloba* a subspecies of *toxicodendron* (Candolle, "Monographic Phanerogamarum," iii., 395; Engler and Prantl, "Die Natürlichen Pflanzen-familien," 1897, 111-5, 168). The only botanical ground for the separation of the two into different species is a slight difference in the shape of their leaflets (Gray, "Synoptical Flora," 1895-7, i., Pt. 1, Fasc. 1-2, 382).

Is the Poison a Glucoside of Rhamnose, Gallic Acid, and Fisetin?—As far as is known to the writer no work has been published on the chemistry of the poisonous principle of poison oak (*Rhus diversiloba*, T. and G.). Because of the very close botanical relationship existing between poison oak and poison ivy (*Rhus toxicodendron*, L.) and because of their identical pharmacological action it has always been held among the medical profession, as well as among botanists, that the poisons were identical. Not only are they similar in pharmacological action, but they are also similar in solubility, rapid oxidation, &c.

In seeking to find out the constitution of the poisonous compound of poison oak the work done on its very closely related plant has been investigated. Perhaps the most recent work is that of Syme, 1906 ("Some Constituents of Poison Ivy Plant," Johns Hopkins University Dissertation, 1906; Acree and Syme, *Am. Chem. Journ.*, 1906, xxxvi., 303, 316), who claims to have found upon a hydrolysis of the poison of *Rhus toxicodendron*, rhamnose, gallic acid, and fisetin.

In an attempt to secure on hydrolysis of the poisonous principle of poison oak the same constituents as Syme obtained from poison ivy the writer was unsuccessful. Therefore, it must be concluded that the poison of *Rhus diversiloba* is not a glucoside of rhamnose, gallic acid, and fisetin.

While we have not repeated the work on the plant Syme experimented with, it seems strange that such closely related plants should have such widely different poisonous principles. It is true that there is often a slight change in the chemical constitution of glucosides, oils, nitrogenous bases, &c., between plants of the same botanical genus, but it is, indeed, an exception where a wide variance occurs, as the results of these experiments would indicate (Pictet and Biddle, "The Vegetable Alkaloids," 114).

Such a difference in the chemical nature of the poisons could hardly be laid to a difference in climate or soil. Poison ivy is found all over Eastern United States as well as in Washington and Oregon. Poison oak is found from the Gulf of California to the Canadian border. Who shall say that it does not endure at least as rigid a climate and surely as mild a one as poison ivy?

Fisetin, gallic acid, and rhamnose, the constituents of Syme's glucoside, are found in large quantities in two plants of the botanical genus to which both poison ivy and poison oak belong, viz., *Rhus cotinus*, L. (Schmid, *Ber.*, 1886, lxxix., 1734), and *Rhus rhodanthema* (Perkin, *Journ. Chem. Soc.*, 1897, lxxi., 1194). It might be supposed from Syme's observations that that these species would be poisonous. As a matter of fact, however, neither of these species is poisonous.

Rhus cotinus yielded, when analysed in 1886 by Schmid (*Ber.*, 1886, lxxix., 1734), a glucoside on water extraction which was called "glycosidgerbsäure des Fisetins" or Fustin tannid. This substance gave, on hydrolysis with alkalis or mineral acids, the same substances which Syme's glucoside contained, viz., fisetin, rhamnose, and gallic acid.

While it cannot be positively denied that some poisonous glucoside may exist which contains fisetin, rhamnose, and gallic acid, yet so far as known there has been no corroboration of Syme's conclusion. All the evidence at hand points towards a non-toxicity of a glucoside of fisetin, gallic acid, and rhamnose.

In repeating the work of Syme the writer used gasoline as an extractive material in preference to ether which Syme used. This selection was made because the writer realised that gasoline did not appreciably dissolve rhamnose, gallic acid, tannin, or fisetin, whereas ether does act as a solvent for gallic acid, tannin (Beilstein, *Organische Chemie*), and fisetin when combined with rhamnose (*Ber.*, 1886, lxxix. 1734). Besides these things ether dissolves many other interfering substances, *e.g.*, chlorophyll (Syme, *loc. cit.*), which gasoline does not.

While both of us worked with a "poisonous tar, wax, or gum," yet there is reason to believe that ours was the purer product. It cannot be denied at present that there may be a poisonous glucoside of fisetin, rhamnose, and gallic acid, but there is certainly strong presumptive evidence that such is not the case. There is not sufficient evidence that the poisonous substance which Syme attempted to decompose was not a complex containing the poisonous body and one or more non-toxic glucosides in addition. These may consist of some combination of fisetin, rhamnose, and gallic acid.

We would suggest, therefore, that the work with *Rhus toxicodendron* be repeated for substantiation and a synthesis be made of the pure poison or poisons. For it seems strange indeed that such closely related plants should have such different poisons.

Experimental Data.

An attempt to verify the results of Syme's hydrolysis was made by the author with the poison of *Rhus diversiloba*.

The poisonous principle in the following experiment was obtained by extracting *chips* or *limbs* in a Soxhlet apparatus with 86° Baumé gasoline, In other experiments the *leaves* have been used and similar results have been obtained. The gasoline was evaporated and the black residue pulverised in a glass mortar. The powdered material was placed with two litres of distilled water in a tall glass cylinder. The black substance was insoluble in water and sank to the bottom of the cylinder. It was thoroughly shaken at least once a day for a week, after which time the aqueous portion was decanted. Two litres of fresh distilled water were now added and the shaking process repeated for another week. At the expiration of this time the aqueous liquid was decanted from about 25 grms. of the black material, and the liquid was evaporated to dryness. The residue, very small—about 3 mgrms. per litre—represented the amount of water-soluble constituents in the black material.

The black material was repeatedly extracted with 95 per cent alcohol. The first portions of the alcoholic extract were coloured light brownish yellow. The later portions of the extract were light yellow, indicating that the chromatic alcohol soluble material had been nearly all extracted. This poisonous alcoholic extract, which amounted to about 800 cc., was heated on the water-bath during working hours for two and one-half days with a solution of 2 grms. of concentrated sulphuric acid in 100 cc. water—to hydrolyse the alcohol-soluble material.

The alcohol was driven off of the solution at the end of the period of treatment. The colours of the solution were as follows:—

Colour of alcoholic extract, light brownish yellow; colour after addition of acid solution, the same; colour of olution after driving off alcohol, the same. When the lcohol was driven off there remained, besides the aqueous olution, a quantity of black tar-like material, insoluble in water.

An alcoholic solution of the tar-like material was extremely poisonous, while the aqueous solution was found to be non-poisonous when applied to tender skin. *In the aqueous solution* should be Syme's so-called hydrolysis products of the poison ivy, viz., fisetin, gallic acid, and rhamnose, as each of these materials is easily soluble in water.

Reactions of the Aqueous Solution.

Rhamnose, or any other reducing sugar, was not present for the following reasons :—

A portion of the solution which had been neutralised to litmus with a sodium carbonate solution gave a slight turbidity when treated with Fehling's solution. The slightest perceptible amount of copper oxide was precipitated, not enough to be a decisive test for reducing sugars.

A portion of the neutralised and also of the unneutralised solution tested with α-naphthol gave a negative test for carbohydrates (Browne, "Handbook of Sugar Analysis," 341). It was found that when the solution was passed through an ordinary filter paper the test gave positive results ; this was due to carbohydrates from the paper.

Gallic acid was not present for the following reasons :—

When a portion of the unneutralised solution was treated with ferric chloride solution a light brown colour was produced, no precipitate. The colour was somewhat deeper than the original solution before treatment. When a drop of sodium carbonate solution was added, a precipitate of ferric hydroxide was formed, the solution filtered from the mass was nearly colourless, being slightly yellowish.

Fisetin was not present, for when a portion of the aqueous solution was shaken with ethyl acetate no colouring matter was extracted from the solution.

Comparison of this Attempted Hydrolysis with the work of Syme.

No similarly coloured solution was formed during the hydrolysis as was mentioned in his work.

No tests indicating gallic acid were obtained by means of ferric chloride as is to be found in the dissertation.

Positive tests for rhamnose or reducing sugars with α-naphthol and Fehling's solution were not obtained. Especial care was taken in the filtrations throughout to use glass-wool instead of filter paper in order that dissolved carbohydrates from the paper would not interfere with the test for rhamnose.

The hydrolysis did not liberate fisetin. This was indicated by the fact that ethyl acetate shaken with the aqueous solution did not extract colouring matter from the solution.

No Optical Activity.

A gasoline solution of the poison, the aqueous solution of possible hydrolytic products, as well as an ethyl acetate solution of the poisonous hydrolytic residue, exhibited *no* evidences of optical activity when observed through a decimetre tube in a triple field saccharimeter. While this does not positively prove the absence of an asymmetric carbon atom, or rhamnose in the poison, it furnishes strong presumptive evidences in that direction.

From the evidence presented above it is concluded that the poison in *Rhus diversiloba* cannot be hydrolysed by means of acid into the compounds, rhamnose, gallic acid, and fisetin.

Summary.

1. *Rhus diversiloba* and *Rhus toxicodendron* are very similar plants ; their only botanical difference lies in a slight difference in the shape of their leaflets.

2. The poisonous principle of *Rhus diversiloba* is not a glucoside of rhamnose, fisetin, and gallic acid.

3. Syme's conclusion that the poison of *Rhus toxicodendron* is a glucoside of fisetin, rhamnose, and gallic acid should be repeated for substantiation for :—

(*a*) It seems strange that two such closely related plants botanically should have such widely different poisons chemically,

(*b*) All three of the so-called constituents of the poison are found in two non-poisonous species of *Rhus*.

(*c*) The natural glucoside of fisetin, rhamnose, and gallic acid is non-toxic.

(*d*) There is not sufficient evidence that a poisonous substance which Syme attempted to decompose was not a complex containing a poisonous body to one or more non-toxic glucosides in addition.

I am indebted to Professors H. C. Biddle and T. Brailsford Robertson for their advice throughout the investigation. – *Journal of the American Chemical Society*, xxxviii., No. 7.

MISCELLANEOUS.

Report of the Corrosion Committee of the Institute of Metals. – Volume xv. of the *Journal of the Institute of Metals* contains the third report of this Committee, in which some important laboratory work is described. The anthors, Messrs. Gibbs, Smith, and Bengough, believe that the experimental work on the causes of corrosion have now reached such a stage that a start can be made upon the investigation of the problem of protection against corrosion. They suggest various means by which it may be minimised ; *e.g.*, by keeping the temperature low, by making the flow of water as smooth as possible, and by removing oxysalts as soon as they are formed.

Citric Acid by Fermentation.—John Albert Martin. —As far back as 1884 it was known that artificial citric acid, resembling the natural substance in all its properties, could be formed in certain conditions by the fermentative action of micro-organisms on carbohydrates. The price of citric acid has advanced over 100 per cent recently, owing to the war and to the destruction of lemon groves in southern Europe by earthquakes and volcanoes. The author, in September, 1915, began a systematic study of the preparation of the acid by fermentation and has now published the results. He found that certain fungi of the Ascomycetes group when allowed to grow on a solution of sugar produce citric acid. Different species of the group of fungi have different activities. The solution containing proper nutrient salts and dextrose (not exceeding 10 per cent) must be neutral or slightly acid and the temperature must be carefully regulated. The production of acid is proportional to the growth, which is dependent upon temperature but independent of light. It is necessary to have an excess of air for the conversion of sugar into acid, and hence the flask for fermentation should be spacious and shallow. When the production of acid has reached about 20 per cent of the sugar used the growth of the plant is stopped, but a greater yield may be obtained by neutralising the acid formed with calcium carbonate, when a yield of 50 per cent may be obtained.—*American Journal of Pharmacy*, August, 1916, lxxxviii., No. 8.

MEETINGS FOR THE WEEK.

Tuesday, 17th.—Institution of Petroleum Technologists, 8. "The Norfolk Oil Shales," by W. Forbes-Leslie.

Wednesday, 18th.—Microscopical, 8. "On certain Parasites of the Mouth in Cases of Pyorrhœa," by H. Pixell Goodrich and M. Mosely. Exhibition of specimens of Volvocaceæ.

THE CHEMICAL NEWS

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PRECISION IN CHEMICAL WEIGHING.

By WILLIAM NORMAN RAE and JOSEPH REILLY.

The facility with which accuracy can be obtained in weighing depends to a large extent on having a good balance properly erected and carefully adjusted. To introduce our subject with at least a brief discussion on these points will not be out of place. The balance room calls for first consideration.

The chief requirements of a balance room are a uniform temperature, good lighting, and freedom from draughts and direct sunshine. If the room is lighted from the north and the balances are placed along the south wall the light falls on the scale and enables it to be seen distinctly, while any radiation from outside falls equally on the two arms, and so is less likely to produce disturbing effects. It is a disadvantage to have the balance table against the outer wall, as the disturbing effects due to bad weather are more pronounced. The desirability of a uniform temperature will be clear from what follows, and in this connection double doors and windows are a distinct advantage. Since a rigid table is essential for accurate work the balance tables are best made entirely of reinforced concrete or of slate slabs supported on brick pillars built up from the floor. If the room is upstairs the supports can be built out from the wall.

For work of the highest accuracy different workers have used various devices. Brauner covered his balance with a thick layer of flannel to shield it from radiation; Briscoe and Little supported the levelling screws of the case on glass plates standing on packets of filter-paper on the stone slab to deaden the effect of vibration of the building (large rubber stoppers can be used for the same purpose); Edgar and Dixon used a cellar as balance room; Manley used a room with a north-east aspect, but it was darkened and then illuminated with artificial yellow light—his balances were placed in steady temperature cupboards built up of plate glass, asbestos, and cotton wool. Crookes was one of the first workers to realise the importance of these factors. The balance he used in the determination of the atomic weight of thallium was kept in a dry room of uniform temperature, free from draughts, artificial heat, or vapours. In other instances he enclosed the balance (an Oertling) in a cast-iron case and regulated the conditions of the air surrounding the balance as required (see *Proc. Roy. Soc.*, 1872). In these latter experiments, as in the case of Manley's, the balance room, or rather the interior of the iron case containing the balance, was dark. The scale was illuminated by a small electric vacuum tube and the readings taken from a distance by a telescope.

The Chemical Balance.

It can readily be shown theoretically that the sensitiveness of a balance is increased by having a long beam, by reducing the mass of the beam, by making the distance of the centre of gravity below the central knife-edge small, and also by use of a long pointer. These conditions, while increasing the sensitiveness, at the same time increase the time of vibration of the beam, and therefore the time occupied in weighing. In general, therefore, a compromise has to be made—some of the sensitiveness has to be sacrificed to reduce the time of swing.

In precision balances, one of the quantities above mentioned—namely, the distance of the centre of gravity below the central knife-edge—is made variable by means of the gravity bob, a nut with milled edges moving on a screw vertically above the centre of the beam and held in position when the required adjustment is made by a locking nut. As the gravity bob is moved up the sensitiveness and time of swing both increase, while if it is put up too high the equilibrium becomes unstable. With long beam balances a time of vibration of about sixty seconds is convenient, whilst with short beam balances it may be reduced to as low as ten seconds. To get the required length of beam together with proper rigidity, but yet without making the beam unduly heavy, a light framework is used instead of a solid bar; this is usually either triangular in shape or may take the form of a girder with a web of light bars. The use of very long beams is not now so popular as it was, because equal sensitiveness with a shorter time of swing can be secured with a short beam and a long pointer. It is recognised, however, that any slight errors in the adjustment of the knife-edges produce greater effects with short than with long beams; in fact it was only by improving these adjustments that the short beam balance became possible.

The three knife-edges should be exactly parallel, and in general are so arranged that they all lie in the same plane, with no load on the balance. If the beam were perfectly rigid the edges would remain coplanar for all loads; in most balances this is not so, and the two end knife-edges fall below the central one for heavy loads. In some cases the beam as a whole may be rigid, but the end knife-edges are carried on light metal projections, which are more easily deflected.

It is sometimes arranged that the terminal knife-edges are above the central one for small loads; then as the load is increased the beam bends slightly, so that the three edges become coplanar, and then with still greater loads the terminal ones fall below the central one. The sensitiveness then increases with the load until the knife-edges are in the same plane and then decreases, thus giving maximum sensitiveness at medium loads. Proctor states that unstable equilibrium is likely to result when the terminal knife-edges are above the central one.

The centre of gravity of the weights and scale pans should always be vertically below the knife-edges; this result is attained by having a loose link between the stirrup and the scale pan, and also by taking care to place the weights centrally on the pan. In some of the best balances the centre of gravity of the pan and its contents is brought below the centre of support as follows:—Two knife-edges are provided at right angles to one another. One of these is the ordinary knife-edge of the beam, the other is usually of cruder construction and is made of metal. This gives a support as nearly frictionless as possible, with freedom in both vertical planes.

The method of fastening the knife-edges to the beam is important, but will only briefly be considered here. Various devices have been used to ensure that the knife-edge and planes are always working in the same relative position—*i.e.*, that release and arrestment do not interfere with their accuracy. Without considering in detail the subject of geometrical slides a reference may be made to the Kelvin "point line and plane" as an example. This device gives a constant relative position despite expansion. In some balances the point line and plane are of metal, in the best they are of agate.

At the centre the frame has two slots, which catch corresponding projections on the bar carrying the central knife-edge, while at each end are two screws with fine points, which engage respectively with a cone and slot on the stirrup which bears the agate plane and the pan. From the back of the plate fixed to the central column rises a short rod, to which is attached the horizontal rod bearing the central agate plane. The arrestment is raised by turning a handle or milled head attached to a horizontal rod which bears two eccentric discs; on one of these rests the end of the sliding rod or a small wheel attached to it, while the other eccentric operates the levers which raise or lower the pan supports. When the arrestment is released the central knife-edge rises just clear of the plane, and at the same time the end planes are lifted from their knife-edges and the pan supports rise and catch the pans. Generally the handle for arresting the beam is in front, although in some balances not of the greatest delicacy it is very conveniently placed at the side to be operated by the left hand, leaving more space for the right hand to add the weights. The method of raising the arrestment rather than the beam is much to be preferred: it makes it easy to start the balance swinging with a small amplitude and avoids disturbing the air to any extent by the motion of the pans.

The pointer is attached to the centre of the beam and tapers to a fine point where it traverses the scale. In some cases the scale divisions are carried to the top of the scale, and the end of the pointer then moves in the plane of the front of the scale and just over the top of it. Generally the fine end of the pointer moves over the front of the scale and very close to it to avoid parallax in reading its position. Another device sometimes used consists of a small rectangular frame bearing a thin cross-wire and fastened to the end of the pointer; the movement of the cross wire is observed through a microscope fixed in the case. With the standard mark on the pointer the reading is dependent on the focussing of the microscope, and this would restrict the range of swing. With the following device for magnifying the range of the pointer this difficulty is overcome. A micro scale is mounted on the pointer upside down. This is observed through a microscope with a spider web in the eyepiece. The magnifying mirror used by Bunge and Kuhlmann is so arranged that it leads to either increased sensitiveness or to reduced time in weighing or to both. A low sensitiveness balance with a microscope is preferred by most workers to the same balance adjusted to a greater sensitiveness and without a microscope.

On the beam itself is the rider scale. The top of the scale is best arranged so that it lies in the same horizontal plane as the three knife-edges. It is a common practice, however, to have the scale above this plane but parallel to it, or even to use the top bar of the beam as the scale, in which case the scale is often not horizontal. The effect of having the scale in a horizontal plane above the knife-edges is to increase the sensitiveness when the rider is put on, but the sensitiveness is not altered by moving the rider from one scale division to another. The effect can be nullified in such a case by placing the rider at the centre of the scale—*i.e.*, directly over the central knife-edge, when it is not being used, instead of raising it off the scale, as is commonly done. In the last case, when the scale is not horizontal when the beam is at rest, the sensitiveness will rise as the rider is moved from the end of the scale towards the centre. The first arrangement is therefore preferable, because the addition or removal of the rider has no effect on the sensitiveness. The effect is a small one, owing to the small mass of the rider, and is only important in very accurate work.

Stas and also Smith state that large flasks after beating or rubbing required six hours to attain this equilibrium; polished platinum reaches a steady state very quickly, while roughened platinum surfaces may take longer than porcelain or glass. Except in work of the highest accuracy this long time is not allowed, a period of about twenty minutes sufficing, in which time the greater part of the change will have occurred, and if exactly the same time period is allowed each time the resulting error will be small.

Some authors—*e.g.*, T. W. Richards, Steele, and Grant—recommend the use of a small quantity of uranium oxide in the case to dispel electric charges produced on glass or quartz apparatus in the process of wiping preparatory to weighing. Glass or quartz weights, it is claimed, become electrified by friction with the velvet lining of the weight-box, and such charged bodies would be attracted by near objects, but it is unlikely that this factor will cause even a small error in weighing.

Weighing.

It is often useless to weigh with very great accuracy; *e.g.*, large pieces of rubber, coal, glass, or platinum often change in weight by some mgrms. in successive weighings. This variation is especially noticed in the weighing of finely divided coal, and several authorities state that in such weighings no desiccating agent should be used in the balance case. In instances like the above the following method of weighing is rapid and satisfactory:—A table is first constructed showing the sensitiveness with various loads. Before the weighing is commenced the pans are wiped with a small camel-hair brush, the case is closed and the beam is carefully released, when the pointer will swing slowly backwards and forwards over the scale (with a little practice this can be done so as to give the pointer any desired amplitude). When the amplitude has fallen to about five scale divisions the readings of the extremities of the swing are taken for five successive swings, the observer sitting directly in front of the balance to avoid parallax in the readings. The first two or three swings are always neglected, to allow the beam to settle down to a steady condition. It is best to number the scale continuously from left to right rather than to call the centre division 0 and those to the right positive and to the left negative. Suppose the middle point of the scale to be numbered 10, and that the following numbers represent the turning points observed in an experiment:—

	Left.	Right.
	9·0	
		11·0
	9·1	
		10·9
	9·2	
		10·95
Mean	9·10	

$$\text{Resting-point} = \frac{9\cdot10 + 10\cdot95}{2} = 10\cdot03$$

The pointer is sometimes viewed through a convex lens placed in front of the scale to magnify the divisions, but this is likely to increase the error due to parallax between the pointer and the scale. When the readings of the turning points have been taken the beam is arrested, care being taken that this is done at the instant the pointer is at the centre of the scale. In this way jarring the knife-edges is avoided; their movement over the planes is also avoided, owing to the fact that while the arrestment pins move vertically the ends of the beam move in the arcs of a circle. The 10 mgrm. rider is now placed on the first division of the scale, with the effect of adding 1 mgrm. to one pan, and the new resting point is found in the same way as the former one. Suppose the value 6·29 is found; this means that the addition of 1 mgrm. shifts the resting point from 10·03 to 6·29, or the sensitiveness with no load is 10·03 - 6·29, *i.e.*, 3·74. The process is then repeated with 10, 20, 30, &c., grms. on each pan, and from the results obtained a curve is constructed with the sensitiveness plotted against the weights.

Damping is of little importance in calculating the resting point, and will only be briefly considered. If a, b, c, &c., be three successive turning points:—

a
b
c
d
e
&c.,

$$\text{then R.P.} = \frac{a+2b+c}{2} = \frac{a+3b+3c+d}{8}, \text{ \&c.}$$

The R.P. in above illustration turns out to be 10·02 instead of 10·03.

We have—

$$b = ae^{-\delta}$$
$$c = ae^{-2\delta},$$

or—

$$\begin{array}{ll} a & \\ & a-\delta \\ a-2\delta & \\ & d-3\delta \\ e-4\delta & \end{array}$$

and hence formulæ.

To weigh an object the method of procedure is as follows: —The object is removed from the desiccator and left in the balance case for twenty minutes. The beam is then released, and the zero determined by the method of oscillations. The object is placed on the left-hand pan, and a large weight is put on the right-hand pan (the weights should be put as near to the centre of the pan as possible, or on releasing the beam the pan will be set in vibration which takes some time to die down), and the handle is turned slightly but only just far enough to see in which direction the beam is going to move; it is unnecessary to completely release the beam. Should the weight be too large the beam is arrested, the weight removed, and the next smaller one is tried, trying each weight in turn until as near as possible equilibrium has been obtained. When this has been done the rider is placed at the fourth division on the scale and tried; if it proves too much it is next tried at a second division, or if too small at the sixth, and so on until the weight to the nearest mgrm. is found. The beam is then released so that it swings with a small amplitude and the turning point of five swings are taken, and from these the rest point (R.P.) is deduced. Sufficient data have now been obtained to ascertain the weight of the object. The method of calculating the exact weight is made clear by the following example:—

Determination of the zero:—

Turning points—

	Left.	Right.
	9·0	
		11·0
	9·1	
		10·9
	9·2	
Mean	9·1	10·95

R.P. 10·03.

With the object on the left pan and 20·57 grms. on the right and the rider on the seventh scale division:—

Turning points—

	Left.	Right.
	9·5	
		12·1
	9·5	
		12·0
	9·6	
Mean	9·53	12·05

$$\text{R.P.} = \frac{9{\cdot}53 + 12{\cdot}05}{2} = 10{\cdot}79.$$

From the sensitiveness curve the sensitiveness for 20 grms. is found to be 3·70.

The R.P. has changed from 10·03 to 10·79; *i.e.* 0·76 divisions.

A charge of 3·70 is the effect of 0·001 grm.

$$\text{,,} \quad 1{\cdot}00 \quad \text{,,} \quad \frac{0{\cdot}001}{3{\cdot}70} \text{ grm.}$$

$$\text{,,} \quad 0{\cdot}76 \quad \frac{0{\cdot}001 \times 0{\cdot}76}{3{\cdot}70} \text{ grm.} = 0{\cdot}0002 \text{ grm.}$$

Since the resting point obtained with the weights on the pan was greater than the zero, the weights were insufficient, and the 0·0002 grm. must be added to the 20·577 grms.; the total weight is thus 20·5772 grms. If the weight is large it is worth while taking the zero after the weighing as well as before and using the mean of the two values.

A centigrade thermometer reading to 0·1 should be kept in the balance case and its reading taken each time a weighing is made; the barometric height should also be recorded; these are required for the vacuum corrections (see later).

Objects must never be weighed until they are at the same temperature as the balance case. Mellor mentions that a platinum crucible weighing 20 grms. appeared to weigh 0·04 grm. heavier cold than when weighed warm. A tentative suggestion is, that owing chiefly to convection currents being set up by the hot body and these acting on that side of the beam, raises it and so makes the object appear too light. A platinum crucible, after heating, should be allowed to remain for twenty minutes in the desiccator and ten minutes in the balance case, whereas a large porcelain crucible, *e.g.*, a Gooch, really requires an hour to reach equilibrium; but this may be shortened to half-an-hour, provided the same time is allowed to elapse throughout any series of experiments.

The authors have noticed that fine powders which have been heated, *e.g.*, precipitated silica, and also Gooch crucibles, steadily gain in weight when transferred from the desiccator to the balance case; this is due to the absorption of moisture and may amount to several mgrms. In weighing an anhydrous powder, therefore, the operations should be carried out as quickly as possible. It may facilitate matters to some extent if the large weghts are placed on the pan before the vessel containing the powder is added; *e.g.*, if a crucible weighing 25 grms. is being used and the weight of the powder is estimated to be 2 grms., 27 grms. may be placed on the pan in readiness. If the object is of such a size that it will conveniently go into a stoppered containing vessel, this can be used with advantage; the vessel being placed in the desiccator with the crucible or boat, and the latter when cooled being placed in the stoppered vessel and transferred to the balance, left the usual twenty minutes to approach equilibrium, and then weighed. The same procedure of course must be adopted in obtaining the weight of the empty boat or crucible.

Powders should be weighed in glass stoppered weighing bottles and then transferred to the reaction vessel, the bottle and the remaining powder being weighed afterwards, the weight of the powder being obtained by difference. Salts containing water of crystallisation should not be placed in the desiccator previous to weighing but should be weighed air dry. Liquids will evaporate in the balance case, and are therefore weighed in stoppered vessels or in one of the numerous weighing pipettes made for the purpose.

When large glass or porcelain vessels have to be weighed, Borda's method of weighing by tares is useful because in these cases the vacuum corrections would otherwise be large, and owing to their uncertainty may cause large errors. (See below). In Borda's method the zero is first determined as usual, and the object to be weighed is placed on the left pan; the tare should be of the same material and of nearly the same weight, volume, and surface area as the object; the tare is placed on the right pan, and small weights are added to one pan to get equilibrium, and the R.P. is calculated. From this we get that the object is equal to the tare, or a small weight "w." After the reaction the object is again weighed against the same tare, and the alteration in weight is thus determined. The tare should receive exactly the same treatment as the object weighed; *i.e.*, if the latter is heated to redness and then cooled in the desiccator for half-an-hour, the tare must be similarly heated and cooled.

(To be continued).

THE DETERMINATION OF FERROUS IRON IN SILICATES BY TITRATION WITH DICHROMATE.

By O. L. BARNEBEY.

The permanganate titration has been used for the determination of ferrous iron in silicates almost, if not quite, exclusively. This study introduces dichromate for this purpose in a method which is proven to be accurate.

A dichromate titration of the ferrous iron obtained by extraction of a silicate with hydrofluoric acid has several points in its favour. A dichromate solution is more stable than the permanganate solution, which is ordinarily used for this purpose. Moderate quantities of hydrochloric acid do not interfere with the dichromate titration, thus allowing the use of this acid, if it is desired, in the extraction process. Dichromate is not as easily reduced by organic matter as is permanganate. However, ferrous iron cannot be titrated accurately with dichromate in a hydrofluoric acid solution. Further, ferrous iron in fluoride solution oxidises so rapidly that a slow titration, such as accompanies the use of an outside indicator on a spot plate, may introduce a considerable error.

Boric acid (Barnebey, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1481) has been found to remove hydrofluoric acid from solution, interaction forming metafluoboric acid. The use of boric acid also permits an accurate titration of ferrous iron to be made with dichromate (Table I.).

Table I.—*Titration of Iron with Dichromate in Hydrochloric and Hydrofluoric Acid Solutions.*

1 cc. $K_2Cr_2O_7$ = 0·006381 grm. FeO. (*a*)
1 cc. $FeSO_4$ = 1·007032 grm. FeO.
(Volume—200 cc.).

	Normality.		FeO (grm.).			Time for development of colour.
	HCl.	HF.	Present.	Found.	Error.	Min.
1.	0·50	—	0·2110	0·2110	—	1
2.	—	0·125	0·2110	0·2108	− 0·0002	1
3.	—	0·625	0·2110	0·1914	−0·0196	0·5
				0·2067	−0·0043	2
				0·2074	−0·0036	3
				0·2080	−0·0030	7
4.	—	3·125	0·2110	0·1659	−0·0451	0·5
				0·1789	−0·0321	1
				0·1914	− 0·0196	2
				Found.		
				Without H_3BO_3.	With H_3BO_3.	
5.	—	0·125	0·2110	—	0·2111	1
6.	—	0·500	0·2110	—	0·2110	1
7.	0·50	0·125	0·2110	—	0·2110	1
8.	0·50	0·625	0·2110	—	0·2109	1
9.	0·50	0·05	0·1567	0·1563	—	1
10.	0·50	0·10	0·1567	0·1566	—	1
11.	0·50	0·15	0·1567	0·1564	—	1
12.	0·50	0·25	0·1567	0·1557	0·1567	1
13.	0·50	0·40	0·1567	0·1552	0·1566	1
14.	0·50	0·50	0·1567	0·1548	0·1567	1
15.	0·50	0·75	0·1567	0·1528	0·1568	1
16.	0·50	1·00	0·1567	0·1492	0·1566	1
17.	0·50	1·50	0·1567	0·1425	0·1567	1
18.	0·50	2·00	0·1567	0·1415	0·1568	1
19.	0·50	2·50	0·1567	0·1400	0·1566	1
20.	—	2·50	0·1567	—	0·1566	1

(*a*). The dichromate solutions used in this work were standardised against pure electrolytic iron, and the ferrous iron solutions were standardised with the dichromate in each series of experiments, using ferricyanide as indicator.

In Experiments 3 and 4 the dichromate was added until, upon placing a drop of the solution in contact with a drop of 0·05 per cent potassium ferricyanide solution, the development of colour on the spot plate was very slow. The time required for the development of the ferrous iron test is designated in the table. More dichromate was then added, and another test applied. The more the dichromate added the longer became the time required for the development of the colour test. These two experiments show that an enormous error may be introduced by the presence of fluorides. In Experiments 5 and 6 boric acid was present and hydrochloric acid absent. In 7 and 8 boric acid was added previous to titration in the presence of hydrochloric acid. Excellent results were obtained in the four experiments. Constant quantities of iron in the presence of constant amounts of hydrochloric acid in constant volume of solution were titrated with variable amounts of hydrochloric acid both with and without the addition of boric acid in excess preceding titration (Experiments 9—20 inclusive). Below approximately 0·15 N the effect of hydrofluoric acid is found to be small when titrating moderate amounts of iron. Above 0·15 N the error becomes progressively larger as the concentration of the hydrofluoric acid increases. The addition of boric acid removes this fluoride effect, and permits excellent results to be obtained even when the concentration of the hydrofluoric acid is 2·5 N.

Sensitiveness of the Ferricyanide Test for Ferrous Iron.

In previous work the author has frequently observed that variation of the strength of hydrochloric acid has a tendency to change the sensitiveness of the ferricyanide test for small amounts of ferrous iron. To ascertain the extent of this effect a series of experiments were performed (Table II.). The effect of hydrofluoric acid was also made a matter of study in this series. In each experiment the acid, with or without added ferric chloride, was diluted to 200 cc. volume and standard ferrous sulphate added until 1 drop of the solution gave the colour test with ferricyanide on a porcelain spot plate.

Table II.—*Sensitiveness of the Ferricyanide Test for Ferrous Iron.*

1 cc. $FeSO_4$ = 0·005222 grm. Fe.
(Volume—200 cc.).

	Normality.		0·1 N $FeCl_3$. Cc.	Fe required. Grm.	Test sensitiveness. One part in—
	HCl.	HF.			
1.	—	—	—	0·0002	1,000,000
2.	0·30	—	—	0·0005	400,000
3.	0·60	—	—	0·0010	200,000
4.	1·20	—	—	0·0019	105,000
5.	1·60	—	—	0·0025	80,000
6.	3·20	—	—	0·0060	33,000
7.	—	0·05	—	0·0020	100,000
8.	—	0·15	—	0·0045	44,000
9.	—	0·25	—	0·0068	30,000
10.	—	0·50	—	0·0094	21,000
11.	—	1·25	—	0 0151	13,000
12.	—	2·50	—	0·0234	8,500
13.	—	—	—	0·0002	1,000,000
14.	0·25	—	5	0·0003	670,000
15.	0·50	—	5	0·0002	1,000,000
16.	1·00	—	5	0·0002	1,000,000
17.	2·50	—	5	0·0004	500,000
18.	—	0·05	5	0·0003	670,000
19.	—	0·10	5	0·0008	250,000
20.	—	0·25	5	0·0022	90,000
21.	—	0·50	5	0·0104	19,000
22.	—	1·00	5	0·0135	15,000
23.	—	2·50	5	0·0140	14,000
24.	—	0·50	10	0·0025	80,000
25.	—	1·00	10	0·0059	34,000
26.	—	0·50	40	0·0010	200,000
27.	—	1·00	40	0·0020	100,000

The column "test sensitiveness" gives the sensitiveness computed upon the basis of actual parts of ferrous iron contained in the solution. In order to obtain the sensitiveness in the spot plate reaction the "test sensitiveness" results should be multiplied by 20, inasmuch as 20 drops of the solution were equivalent to 1 cc., and only a single drop of the solution was removed for the test with ferricyanide. One minute was the time allowed for the colour to develop. Preliminary study had indicated that not less than 0·04 or more than 0·10 per cent potassium ferricyanide gives the best results in the test for ferrous iron. In the tests here recorded three series of tests were used as checks upon each other, involving the use of 0·04, 0·06, and 0·08 per cent potassium ferricyanide solutions.

Experiments 1—6 and 7—12 show a progressive lowering of the sensitiveness of the ferrous iron test as the normality of the hydrochloric and hydrofluoric acid increases. However, the addition of ferric iron to the solution (Experiments 14—27) permits a more accurate test to be made. (The ferric chloride was entirely free from any trace of ferrous iron). Sulphuric and phosphoric acids give an effect similar to hydrochloric acid. Using 2·5 N sulphuric acid 0·004 grm. of iron was required in 200 cc. vol. to give the ferrous iron test on the spot plate. This corresponds to a solution sensitiveness of one part in fifty thousand and a spot plate sensitiveness of one part in a million. With 2·5 N phosphoric acid (computed on the basis of three replaceable hydrogen atoms), 0·006 grm. of iron was necessary, corresponding to one part in thirty-three thousand and six hundred sixty thousand parts for the solution and spot plate sensitiveness, respectively. The addition of ferric chloride to the solution or spot plate, especially the latter, brings out the test with a very small amount of ferrous iron, 0·0002 grm. being easily detected, hence yielding a solution sensitiveness of one part in a million and a spot plate sensitiveness of one part in twenty million parts of solution. Other salts such as sodium, ammonium, potassium, barium, and aluminium chlorides do not have an effect similar to ferric chloride. It does not seem improbable that the ferrous chloride in strong acid solution reduces in part the ferri to ferrocyanide (see also Hofmann, Heine, and Höchteln, *Ann.*, 1904, cccxxxvii., 1). The ferrocyanide then reacts with the ferric iron present to form a salt similar to or identical with "prussian blue." "Prussian blue" has a tendency to decompose in hydrochloric acid solution forming ferric chloride and hydroferrocyanic acid. Now the addition of ferric iron to such a solution tends to form a ferriferrocyanide by mass action, hence causing the colour to reappear. When the hydrochloric acid is weak the reaction on the spot plate proceeds normally, yielding a ferrous ferricyanide. However, the reactions are undoubtedly complex in character, as indicated by the differences of colours, green to blue, obtained on the spot plate. It matters not which blue or greenish blue is formed if the appearance of colour can be obtained by the presence of a very slight excess of ferrous iron in such a manner as to constitute a reliable test.

The effect of diminishing sensitiveness of the ferrous iron test in strong hydrochloric and hydrofluoric acid solutions was tried in the titration of small amounts of iron. In this series of experiments the standard solutions of ferric chloride, ferrous chloride, and potassium dichromate were approximately 0·1 N (Table III.).

In the presence of 2·5 N hydrochloric acid small amounts of ferrous iron cannot be titrated directly with accuracy (Experiments 1, 4, 5, and 8). Experiments 2, 6, and 9 show that the addition of ferric chloride to the solution of ferrous iron permits a correct titration to be made, even when the hydrochloric acid is 2·5 N. As the quantity of ferrous iron to be titrated increases, thus forming more ferric iron in solution, the titration becomes more accurate. Experiments 11, 12, 13, and 14 indicate that amounts of ferrous iron above 0·05 to 0·10 grm. can be titrated in even 2·5 N hydrochloric acid with safety. Experiments 15, 16, 17, and 18 show that 0·50 N acid is not detrimental when above 0·03 grm. of iron is being titrated. With less concentrations of acid much less ferrous iron could be accurately determined. The addition of ferric chloride to the fluoride solution has a tendency to improve the accuracy of the titration, yet not to a sufficient degree to make the titration reliable (Experiments 19—32). The addition of a drop of ferric chloride to each drop of indicator on the spot plate before or after adding the drop of solution to be tested gave a much more accurate result in Experiments 21, 24, 27, 30, and 32. However, this required careful observance for the end-point, which was a trifle obscure because of a very slight green tinge remaining after the titration was completed. However, the addition of boric acid removes the hydrofluoric acid, thus permitting an accurate titration of small amounts of ferrous iron to be made the same as when larger amounts are involved (Experiments 33—37, see Table I.).

Table III.—*Effect of Strong Hydrochloric and Hydrofluoric Acids on the Titration of Small Amounts of Ferrous Iron.*

	Normality.		0·1 N $FeCl_3$.	Fe (grm.).		
	HCl.	HF.	Cc.	Present.	Found.	Error.
1.	2·50	—	—	0·0057	0·0027	—0·0030
2.	2·50	—	10	0·0057	0·0055	—0·0002
3.	0·25	—	—	0·0057	0·0057	—
4.	2·50	—	—	0·0113	0·0064	—0·0049
5.	2·50	—	—	0·0170	0·0156	—0·0014
6.	2·50	—	10	0·0170	0·0170	—
7.	0·25	—	—	0·0170	0·0170	—
8.	2·50	—	—	0·0284	0·0275	—0·0009
9.	2·50	—	10	0·0284	0·0285	+0·0001
10.	0·25	—	—	0·0284	0·0282	—0·0002
11.	2·50	—	—	0·0567	0·0564	—0·0003
12.	2·50	—	—	0·0567	0·0565	—0·0002
13.	2·50	—	—	0·1134	0·1135	+0·0001
14.	2·50	—	—	0·1134	0·1135	+0·0001
15.	0·50	—	—	0·0284	0·0285	+0·0001
16.	0·50	—	—	0·0567	0·0565	—0·0002
17.	0·50	—	—	0·1418	0·1416	—0·0002
18.	—	—	—	0·2268	0·2268	—
19.	—	0·25	—	0·0057	0·0004	—0·0053
20.	—	0·25	5	0·0057	0·0020	—0·0037
21.	—	0·25	(*a*)	0·0057	0·0054	—0·0003
22.	—	0·25	—	0·0113	0·0074	—0·0039
23.	—	0·25	5	0·0113	0·0088	—0·0025
24.	—	0·25	(*a*)	0·0113	0·0113	—
25.	—	0·50	—	0·0113	0·0034	—0·0079
26.	—	0·50	5	0·0113	0·0074	—0·0039
27.	—	0·50	(*a*)	0·0113	0·0114	+0·0001
28.	—	1·00	—	0·0113	—	—0·0113
29.	—	1·00	5	0·0113	0·0025	—0·0088
30.	—	1·00	(*a*)	0·0113	0·0084	—0·0029
31.	—	2·00	5	0·0113	0·0004	—0·0109
32.	—	2·00	(*a*)	0·0113	0·0059	—0·0054
33.	—	2·50	H_3BO_3 added	0·0057	0·0057	—
34.	—	2·50	,,	0·0113	0·0114	+0·0001
35.	—	2·50	,,	0·0170	0·0171	+0·0001
36.	—	2·50	,,	0·0284	0·0286	+0·0002
37.	—	2·50	,,	0·0284	0·0286	+0·0002
38.	—	2·50	,,	0·0567	0·0570	+0·0003

(*a*) Drops of the ferric chloride solution were added to the ferricyanide on the spot plate.

From the preceding work it is recommended that not more than 5 or at the most 10 cc. of concentrated hydrochloric acid be present in a volume of 200 cc. when small amounts of iron are to be titrated. Inasmuch, as the use of 10 cc. has no advantage over 5 cc., the latter amount should be employed. Boric acid when added to solutions containing hydrofluoric acid removes the latter and permits a quantitative determination of the iron to be made, whether the iron is present in small or large amounts.

Analysis of Silicates for Ferrous Iron.

In a previous article (Barnebey, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1191) ferrous iron solutions containing fluoboric acid were shown to be quite stable in the presence of the air. Since the use of boric acid permits a correct titration to be made, the method previously outlined (*loc. cit.*) can be modified, using dichromate instead of permanganate for the standard oxidising solution. In Series IV. the samples were decomposed according to the method referred to above, using 10 cc. of hydrochloric acid, sp. gr. 1·2 (sulphuric acid can be used if desired), and 10 to 20 cc. of hydrofluoric acid of 48 per cent strength. A convenient strength of dichromate was found to be 1 cc. = 0·001 grm. FeO. A 0·05 per cent solution of potassium ferricyanide was used as indicator on a spot plate, one drop being placed on each spot. When the end-point had apparently been reached, two or three drops of the solution being titrated were used for the final test for ferrous iron in the spot plate reaction, thus increasing the accuracy of the test.

TABLE IV.—*Analysis of Silicates for Ferrous Iron.*

Silicate No.	Sample. Grms.	Per cent FeO found by— $KMnO_4$.	$K_2Cr_2O_7$.
1.	1	1·10	1·02
2.	2	0·51	0·51
3.	1	13·80	13·70
4.	1	14·41	14·38
5.	1	6·49	6·40
6.	1	5·47	5·47

In the analysis of Samples 1 and 2 the solutions had to be filtered to remove suspended organic matter in order to permit titration with permanganate, yet no trouble was encountered in titrating with dichromate without filtration. Samples 3—6 inclusive did not contain organic matter. All of these results are average results of closely agreeing duplicating analyses.

Conclusions.

1. The concentration of acid should be small when titrating small amounts of iron with dichromate, using ferricyanide as indicator on the spot plate. If the concentration is quite large ferric chloride should be added to give a sharper colour change on the spot plate.

2. Boric acid counteracts the influence of hydrofluoric acid in the dichromate titration of ferrous iron, and hence addition of this reagent to the hydrofluoric acid extraction of the silicate yields a solution in which the ferrous iron can be accurately titrated with dichromate, using ferricyanide as indicator on a spot plate.—*Journal of the American Chemical Society*, xxxvii., No. 8.

THE ESTIMATION OF VANADIC ACID AFTER REDUCTION BY METALLIC SILVER.

By GRAHAM EDGAR.

AMONG the many reactions of vanadic acid to be found in the literature, that with metallic silver seems to have been almost overlooked by the numerous investigators who have studied the element vanadium. The only reference which the writer has been able to find bearing at all on this subject is the statement in a paper by Campbell and Griffin (*Journ. Ind. Eng. Chem.*, 1909, i., 661) that "silver, lead, copper, and other elements were tried (as reducing agents on mixed uranyl and vanadyl solutions), but . . . offered no advantages for this purpose." It is true that Perkins (*Am. Journ. Sci.*, [4], xxix., 540) reduced vanadic acid to the tetroxide by the action of hydriodic acid and metallic silver, but he considered that the function of the silver was merely that of absorbing the iodine set free in the reaction, and the possibility of any direct action between the silver and vanadic acid seems not to have been thought of.

That silver should be capable of reducing pentavalent vanadium to tetravalent could be predicted with a considerable degree of certainty by consideration of the values obtained by Rutter (*Zeit. Anorg. Chem.*, 1907, lii., 368) for the oxidising potentials of solutions of vanadic acid, and also from the fact that silver is capable of reducing ferric salts, which are less easily reduced than solutions of vanadic acid. That the reduction cannot proceed further than the tetravalent stage (as it does in the case where zinc, magnesium, or aluminium is used as the reducing agent) could also be predicted from the fact that divalent and trivalent vanadium salts precipitate metallic silver from solutions of silver salts (Rutter, *loc. cit.*). We should expect therefore that the reaction—

$$Ag + VO^{+++} \rightarrow Ag^{+} + VO^{++}$$

should be strictly quantitative, an expectation which is fully confirmed by the results given in this paper.

The course of the reaction can obviously be measured in three ways:—(*a*) From the loss in weight of the metallic silver (if a weighed excess is used to effect the reduction); (*b*) by estimation of the dissolved silver (for example, by titration with standard NH_4CNS solution); and (*c*) by oxidimetric estimation of the reduced vanadium, say with standard $KMnO_4$. Provided the reaction is strictly quantitative any one or all of these methods might be used for the quantitative estimation of vanadium.

To test the validity of these conclusions a series of experiments was carried out to determine the conditions, if any, under which a quantitative reduction of pentavalent vanadium to tetravalent might be expected.

Reagents and Apparatus.

Solutions of pure sodium vanadate (free from chloride) were carefully standardised against $KMnO_4$ after reduction with sulphur dioxide, and also by the very accurate method of Holverscheit (*Inaug. Diss.*, Berlin, 1890).

Potassium permanganate, approximately 0·05/N, was standardised against sodium oxalate.

Ammonium thiocyanate, approximately 0·05/N, was standardised against 0·1/N silver nitrate.

Metallic silver was prepared by electrolysis of a silver nitrate solution, using a platinum anode enclosed in a porous cup, and a fine platinum wire suspended near the top of the solution as cathode. Under these conditions if a moderately heavy current is passed through the solution the silver is deposited as a "bush" of very fine crystals, which drop continually from the cathode to the bottom of the beaker, and which can be later removed by filtration. The finely divided crystals were boiled with dilute sulphuric acid in order to remove any impurities which might be soluble in this medium and were then filtered off through an alundum crucible, washed, and ignited at low red heat. In certain of the preliminary experiments other forms of silver were used—for instance, that formed by precipitation by zinc dust from dilute silver nitrate solution, or by igniting silver oxide, or in one case a spiral of pure fine silver wire. Mention is made of this in later discussion.

All pipettes and burettes used had been calibrated carefully and carried certificates of accuracy, and the greatest care was taken in making all measurements and readings. In all titrations the amount of the reagent necessary to produce the colour change of the end-point was determined by "blank" experiments and the readings were corrected accordingly. The amount was usually between 0·03 and 0·05 cc.

Experimental Results.

After certain preliminary experiments, which will not be recorded here, a number of determinations were made as follows:—

TABLE I.

No.	V_2O_5 taken. Grm.	Loss Ag. Grm.	$KMnO_4$ N/20×1·4212. Cc.	NH_4CNS N/20×0·9862. Cc.	V_2O_5 calc. from Ag.	V_2O_5 calc. from $KMnO_4$.	V_2O_5 calc. from NH_4CNS.	Mean error. Grms.
1.	0·0702	0·0830	10·85	15·65	0·0701	0·0702	0·0702	0·0000
2.	0·0702	0·0832	10·85	15·68	0·0702	0·0702	0·0703	0·0000
3.	0·0702	0·0828	10·87	15·60	0·0700	0·0700	0·0700	−0·0001
4.	0·1260	0·1492	19·50	28·10	0·1260	0·1261	0·1260	0·0000
5.	0 1260	0·1497	19·50	28·15	0·1264	0·1261	0·1262	+0·0002
6.	0·1260	0·1490	19·50	28·20	0·1259	0·1261	0·1264	+0·0001
7. (*a*)	0·1260	0·1490	19·50	28·10	0·1259	0·1261	0·1260	0·0000

(*a*) Reduced with silver wire; see below.

TABLE II.

No.	V_2O_5 taken. Grm.	$KMnO_4$ N/20×1·4212. Cc.	V_2O_5 found calc. from $KMnO_4$. Grm.	NH_4CNS N/20×0·9862. Cc.	V_2O_5 found calc. from NH_4CNS.	Mean error. Grm.
1.	0·0702	10·85	0·0702	15·65	0·0702	0·0000
2.	0·0702	10·90	0·0704	15·70	0 0704	+0·0002
3.	0·0702	10·85	0·0702	15·68	0·0703	+0·00005
4.	0·1260	19·48	0·1259	28·10	0 1260	−0·00005
5.	0·1260	19·50	0·1261	28·15	0·1262	+0·00015
6.	0·1260	19·50	0·1261	28·10	0·1260	+0·00005

Carefully measured portions of a standard solution of sodium vanadate were acidified with about 2 cc. of concentrated H_2SO_4, diluted to about 75 cc., and treated with 1 to 2 grms. of metallic silver, the exact weight of which had been previously determined. The small flasks containing the solutions were then placed upon a quartz plate, acd the solutions were boiled gently for twenty minutes, or in some cases for one-halt hour. Usually the boiling was continued for about ten minutes after the appearance of the pure blue colour which signifies practically complete reduction of the vanadium. The solutions were then filtered upon asbestos in weighed perforated porcelain crucibles, and the residue of silver was washed with hot water. The crucibles were then placed inside of a larger nickel crucible and heated therein for about one-half hour, the outer crucible being subjected to the full heat of a large Bunsen burner. Under these conditions the inner porcelain crucible is at very low red heat. After cooling in a desiccator the crucibles were weighed and the loss of weight ot the silver was calculated.

The filtrates from the silver, containing all of the vanadium in the tetravalent condition, together with the dissolved silver, were titrated hot with 0·05/N $KMnO_4$. At the completion of this titration the solutions were cooled and titrated for silver with 0·05/N NH_4CNS, after the addition of ferric alum as indicator.

The amount of vanadic acid present was calculated (*a*) from the loss in weight of the metallic silver, (*b*) from the permanganate titration, and (*c*) from the silver equivalent to the thiocyanate titration. The results given in Table I. show that the reaction is strictly quantitative, and that not only the gravimetric method but also the volumetric ones are very accurate measures of the amount of vanadic acid present.

The value of these results is obvious. They afford an accurate and simple *gravimetric* method for the estimation of vanadium, which can in the same operation be checked by *two volumetric* estimations with very little additional trouble. Furthermore, if the gravimetric estimation is not desired the operation can be very materially shortened and still permit the employment of the two volumetric estimations. In Table II. are given the results of experiments in which the acid vanadate solutions were heated as above with unweighed amounts of metallic silver, filtered through paper or asbestos, and the filtrates titrated first with permanganate and then with thiocyanate, as in the first set of experiments.

The results as given in Table II. show that vanadic acid can be very accurately determined by titration with permanganate or thiocyanate, or both, after reduction by metallic silver.

Discussion of Factors Influencing the Completion of the Reaction (based partly upon the above experiments and partly upon the preliminary experiments, not here recorded):—

Time.—The time necessary for complete reduction varied, naturally, with the total amount of vanadium present, with the amount of silver used, and with its state of subdivision. With as much as 2 grms. of finely divided crystalline silver complete reduction of about 0·1200 grm. of vanadic acid occurred after ten minutes' boiling. On the other hand, when only 0·5 grm. of silver was used reduction in some cases was incomplete after as much as one-half hour's boiling. The influence of the state of subdivision of the silver was shown by an experiment in which about 1·5 grm. of fine silver wire was used as the reducing agent. In this case the gravimetric and volumetric estimation (Table I., No. 7) showed that reduction was complete, but this was only after an hour's boiling. The best practice seemed to be to continue boiling gently for about ten minutes after the solution had become a pure blue in colour. Longer boiling, though unnecessary, is not harmful. Certain of the preliminary experiments showed that heating on the water-bath for about two hours could usually be substituted for the boiling, but the results were not quite so certain.

Preparation of Silver.—No appreciable difference could be observed in the action of electrolytic silver, silver reduced by zinc, and silver prepared by heating the oxide, provided the purity was the same, and provided that preliminary treatment with dilute sulphuric acid was given. The electrolytic silver is, however, recommended as being more apt to be pure and as giving somewhat more uniform results. It is easily prepared by the method given above.

Acidity.—The acidity of the solutions was varied between 0·5 cc. and 3 cc. of concentrated H_2SO_4 in a total volume of 75 cc. No very marked differences in behaviour were observed, but somewhat more uniform results were obtained when 1 to 2 cc. in 75 cc. were used.

The reduction takes place readily when hydrochloric acid is used instead of sulphuric. In this case the dissolved silver is precipitated as chloride, and the vanadic acid present may be calculated from the *increase* in weight of the silver used for the reduction, as well as by permanganate titration of the filtrate. The gravimetric method is not quite so accurate as when loss of weight is determined, for of course the increase of weight due to chlorine is only about one-third of the decrease in weight caused by the solution of an equivalent amount of silver. Furthermore, the permanganate titration in the hot solution containing hydrochloric acid is not so accurate as in the presence of sulphuric acid alone, even when all precautions are observed. If it is desired, however, to determine vanadium in a solution containing hydrochloric acid, the silver reduction followed by permanganate titration may be used with a fair degree of accuracy. A better method is to remove the hydrochloric acid with silver sulphate in slight excess and then determine vanadium as described above for solutions containing sulphuric acid. Either the gravimetric method or the permanganate titration may be employed, and even the thiocyanate titration also, provided a blank is run to determine the silver already present.

Nitric acid must not be present for obvious reasons, nor any other substance acted upon by finely divided silver under the conditions of the experiment. The application of the reaction to the determination of vanadium in technical products and in the presence of other substances will be the subject of further investigation.

Filtration.—Where the gravimetric method is to be carried out filtration through asbestos in a perforated porcelain crucible (or through alundum) is far preferable to filtration through paper. Where only the volumetric processes are to be carried out filtration through paper is probably more convenient. It is even possible to wash the silver residue by decantation entirely, but filtration in this particular case is so rapid that decantation gains no time, and there is always the risk that fine particles of silver may be carried into the solution to be titrated, and thus spoil the determination.

Accuracy.—The accuracy with which duplication of results can be obtained is very unusual. This is especially true of the permanganate titration, where the writer had had as many as six consecutive titrations show no readable difference in the volume of permanganate used. Slightly greater variations were obtained in the thiocyanate titration, but here also the results are excellent. The writer has had experience with nearly all of the standard methods for the estimation of vanadium, and has obtained better results with the method proposed here than with any other of his experience. The fact that three check determinations may be made on the same solution should make the method admirably adapted to the exact standardisation of vanadic acid solutions or to other cases where high accuracy is desired.

Another useful feature of the method is the opportunity which it offers for the gravimetric standardisation of permanganate solutions against metallic silver, or of comparing permanganate and thiocyanate solutions against one another. For this purpose complete reduction of the vanadic acid is not necessary, as the three factors—loss of weight of silver, permanganate titration, and thiocyanate titration—are always strictly proportional, regardless of the extent to which the vanadium is reduced.

Summary.

Vanadium is quantitatively reduced from the pentavalent to the tetravalent condition by metallic silver in acid solution under proper conditions.

The reaction may be used to determine vanadium (*a*) gravimetrically, from the loss in weight of the silver; (*b*) oxidimetrically, by titration with standard potassium permanganate; or (*c*) by titration of the dissolved silver with ammonium thiocyanate. All of these operations may be carried out on the same solution and serve to check each other.

The results are of the highest order of accuracy.

The reactions may be also used for the standardisation of permanganate solutions against silver and of permanganate and thiocyanate solutions against each other.—*Journal of the American Chemical Society*, xxxviii., No. 7.

A MODIFICATION OF McCRUDDEN'S METHOD FOR CALCIUM, FOR THE ESTIMATION OF CALCIUM AND STRONTIUM IN THE PRESENCE OF PHOSPHORIC ACID AND A SMALL AMOUNT OF IRON.

By O. B. WINTER.

THE method generally used in estimating calcium and strontium when both are present in a solution is to precipitate them as the oxalates, burn to the oxides, change to the nitrates, separate the calcium nitrate from the strontium nitrate by means of absolute alcohol and ether, and then determine each element separately (U.S. Dept. of Agr., Bureau of Chemistry, *Bull.* 162, 44). If phosphoric acid and iron are also present in the solution with the calcium and strontium salts the separation becomes much more difficult, since calcium, strontium, and iron phosphates are quite insoluble in a neutral or alkaline solution. In this latter case the phosphoric acid and iron are removed before the calcium and strontium are determined. This is usually accomplished by precipitating the phosphoric acid as ferric phosphate and the excess of iron as ferric subacetate (Perkin, "Methods in Qualitative Analysis," p. 76). However, when there is a large amount of phosphoric acid in the solution this method becomes tedious, because the bulky gelatinous precipitate formed causes the solution to filter very slowly, and it is almost impossible to wash all of the calcium and strontium salts out of this precipitate.

McCrudden has worked out a method for "the quantitative separation of calcium and magnesium in the presence of phosphoric acid and small amounts of iron, devised especially for the analysis of foods, urine, and feces" (*Journ. Biol. Chem.*, 1909, vii., 83). By this method the calcium is precipitated very slowly as the oxalate in a boiling solution containing a small amount of free hydrochloric acid. This gives rise to a condition in which the calcium oxalate comes down very coarsely crystalline, and apparently no soluble salts are carried down by occlusion.

The above method was found accurate for the estimation of calcium, but in trying it out on a strontium solution it was found that this element ran low, but not so much so as was anticipated. Several different modifications of the method were attempted, and finally it was shown that the addition of alcohol would ensure complete precipitation of strontium. The following method gave very satisfactory results for both calcium and strontium:—

Dilute the solution containing the calcium or strontium or both to about 200 cc. and add a few drops of alizarin and ammonium hydroxide until the solution is faintly alkaline. Now add dilute hydrochloric acid until the solution is faintly acid. To this solution add 10 cc. of 0·5/N hydrochloric acid and 10 cc. of 2·5 per cent oxalic acid and boil until the precipitate becomes coarsely granular. Then add saturated ammonium oxalate solution, a few drops at a time with constant stirring, until about twice the amount necessary to precipitate all the calcium and strontium has been added. Cool the solution, add (with constant stirring) 8 cc. of 20 per cent sodium acetate solution and about 15 cc. of 95 per cent alcohol, and allow to stand from four to eighteen hours. Filter and wash the precipitate a few times with 1 per cent ammonium oxalate solution, several times with 1 per cent ammonium oxalate solution containing 20 per cent by volume of alcohol, and finally a few times with water containing 20 per cent by volume of alcohol. Now burn the precipitate to the oxide, dissolve in nitric acid, dehydrate, separate the calcium nitrate from the strontium nitrate by means of absolute alcohol and ether, and determine each element in the usual manner (U.S. Dept. of Agr., Bureau of Chemistry, *Bull.* 162, 44).

That this modified method gives quantitative results is

Results by Modified McCrudden Method.

No.	$P_2O_5 + Fe_2O_3$	Grm. calcium oxide (CaO). Present.	Grm. calcium oxide (CaO). Found.		Grm. strontium oxide (SrO). Present.	Grm. strontium oxide (SrO). Found.		
1.	Absent	—	—	—	0·0493	0·0494	0·0496	0·0498
2.	Absent	—	—	—	0·1464	0·1460	0·1467	—
3.	Present	—	—	—	0·0991	0·0995	0·0994	—
4.	Present	0·0908	0·0907	0·0911	—	—	—	—
5.	Absent	0·1004	0·0997	0·1003	0·0732	0·0728	0·0730	—
6.	Present	0·0454	0·0450	—	0·0495	0·0490	—	—

shown in the accompanying table, which gives the analyses of synthetic solutions of calcium and strontium salts. The amount of calcium in these solutions was determined by precipitating it as the oxalate in a neutral solution and then burning to the oxide (Treadwell-Hall, "Analytical Chemistry," "Quantitative Analyses," 1st Ed., 1909, ii., 65), after first removing the phosphoric acid with ferric chloride (Perkin, "Methods in Qualitative Analysis," p. 76) and the excess of iron as ferric sub acetate. The strontium in the solutions was estimated as the sulphate (Treadwall-Hall, "Analytical Chemistry," "Quantitative Analyses," 1st Ed., 1909, ii., 66), and calculated to the oxide).

Summary.

1. McCrudden's method, with the modifications given in this paper, may be used for determining calcium of strontium.

2. This modified McCrudden method is accurate and convenient for determining calcium and strontium when both are present in a solution containing phosphoric acid and a small amount of iron.—*Journal of Industrial and Engineering Chemistry*, viii., No. 7.

THE RATE OF AMMONIA DISTILLATION FROM WATER.

By F. W. BRUCKMILLER.

In the determination of the ammoniacal nitrogen in waters the quantity of ammonia obtained depends upon a number of factors, principal among which are the volume of the distillate saved and the rate at which the ammonia comes over.

Regarding this matter Wanklyn ("Water Analysis," 1896, 43, the originator of the method, says:—

"The recommendation has been given to nesslerise only the first 50 cc. of the free ammonia and to throw away the next 150 cc. Formerly it was our custom to nesslerise all four 50 cc. tubes for the free ammonia, but that was a useless trouble, inasmuch as the first 50 cc. invariably contained three-fourths of the total free ammonia. The rule is, therefore, to nesslerise the first 50 cc. of the distillate and then add one-third. In the instance of the albuminoid ammonia it is necessary to nesslerise each separate 50 cc. of the distillate (4) and to add the amounts together in order to arrive at the total albuminoid ammonia."

Mason ("Examination of Water," 1913, 62), who has used the method extensively, says:—

"Usually four 50 cc. tubes will be sufficient to carry off all the free ammonia, but it is the author's custom always to distil off six."

Stocks ("Water Analysis," 1912, 11), says:—

"In distilling ordinary waters practically the whole of the ammonia will be present in the first 100 cc., but with sewages the whole of the ammonia may not have been obtained even after distilling 300 cc., and it is therefore necessary in such cases to allow the retort to cool, make up to the original volume with distilled water, and continue the distillation. The albuminoid ammonia being formed by the oxidation of organic matter, is not evolved so quickly as the free ammonia, hence it may be necessary to distil several 100 cc. portions before it ceases to be evolved."

"The Standard Methods of Water Analysis" (1912 edition) recommends the collection of three 50 cc. portions for the free ammonia, and at least four, preferably five, 50 cc. portions for albuminoid ammonia. This procedure we were using until we saw an advance copy of the Revision of the Standard Methods and learned that it was recommending a collection of four 50 cc. Nessler tubes in the distillation of the free ammonia and five in the case of albuminoid ammonia.

In order to see what influence this procedure would have upon the results obtained we began a statistical study of the quantities of ammonia collected in each tube, as well as the total amount obtained. The results of this study are herein contained.

We have been following the revised procedure for several months, using it on all classes of water. The total number of waters examined was between 500 and 1000; the free ammonia varied from 0·002 to 2·0 parts per million, and the albuminoid from 0·002 to 4·0 parts per million. A compilation of all of the results, with regard to amount and rate of ammonia distilling, were made, and the conclusions obtained were as follows:—

Nitrogen as Free Ammonia.

(Fourth tube averages 5 per cent of the total nitrogen).

76 p.c. of the waters had 100 nitrogen in three tubes.
24 ,, ,, ,, 95 ,, ,, ,,
50 ,, ,, ,, 50 to 55 nitrogen in one tube.
20 ,, ,, ,, 65 to 70 ,, ,, ,,

Nitrogen as Albuminoid Ammonia.

(Fifth tube averages 5 per cent of the total nitrogen).

75 p.c. of the waters had 100 nitrogen in four tubes.
25 ,, ,, ,, 95 ,, ,, ,,
30 ,, ,, ,, 50 to 60 nitrogen in one tube.
20 ,, ,, ,, 60 to 70 ,, ,, ,,

Those waters which had 5 per cent of the nitrogen in the last tube had a total nitrogen content of either free or albuminoid ammonia of 1 part per million or more of nitrogen. Since ordinary waters, unless grossly polluted, contain less than 1 part per million of nitrogen as free or albuminoid ammonia, we can conclude that the collection of a fourth tube in the free ammonia determination and a fifth in the albuminoid determination under ordinary circumstances is not necessary. Furthermore, the average per cent found in the last tube, including all samples, was only 5 per cent of the total nitrogen.

In a water containing less than 1 part per million the maximum error is 0·05 part per million; in a water containing 4 parts per million, the maximum amount found in the waters examined, the error is 0·2 part per million. In other words, in one case we would report 0·95 p.p.m. of nitrogen and in the other 3·80. However, since the ammonia determination is not quantitative and the results are used only as a basis for determining pollution, the question to be decided is whether or not the error of 0·05 p.p.m. in one case and 0·2 in the other would cause a change of judgment. We think it would not; that is, a water with 1 p.p.m. of nitrogen would stand as good a chance of being condemned as one containing 0·95 p.p.m. if all the other evidences pointed towards contamination.

We conclude, therefore, from this study that in order to get sufficient information upon which to base a judgment it is not necessary in ordinary routine water analysis to nesslerise more than three 50 cc. portions for free ammonia and four 50 cc. portions for albuminoid ammonia. —*Journal of Industrial and Engineering Chemistry*, viii., No. 7.

ON PRECIPITATION OF MANGANESE.

By GREGORY TOROSSIAN.

It may be of considerable interest to chemists to note that in precipitating manganese by ammonium hydroxide and an oxidiser that sodium and hydrogen peroxides may be used in the place of bromine or bromine water now so generally used.

Sodium peroxide added to a manganese solution precipitates the dark brown manganic hydroxide similar to the precipitate with ammonia and bromine water. Sodium peroxide supplies both the alkali, NaOH, and the oxidiser, oxygen. The powdered Na_2O_2 in small quantities is added to the hot manganese solution until the reaction is alkaline. This precipitates all of the manganese as a dark brown manganic hydroxide in a granular form which quickly settles. If the introduction of sodium into the solution is objectionable, hydrogen peroxide should be used. In such cases a few drops of a 10 per cent hydrogen peroxide solution are added to the manganese solution. After heating to boiling, ammonia is added until the solution is strongly alkaline. Dark brown manganic hydroxide is instantly precipitated. The hydrogen peroxide must be added to the manganese solution before the ammonia is added, otherwise the manganese is incompletely precipitated as a yellow-brown precipitate which is very difficult to filter.

These reagents have many advantages against the use of bromine, as they do not produce annoying fumes, do not increase the volume of the solution, and are far more effective and cheaper than bromine, as only small quantities are necessary to oxidise manganese.—*Journal of Industrial and Engineering Chemistry*, viii., No. 7.

MANCHESTER AND THE DYE-STUFF INDUSTRY.

Scheme for Advanced Training and Research.

After two years of war the Government and the British public have come to realise that Great Britain can no longer do without a well-developed organic chemical industry upon which she may rely for her supply of explosives, dye-stuffs, and synthetic drugs. The Government has shown its appreciation of the national importance of research on these and kindred subjects by the establishment of a Committee of the Privy Council to administer special grants in aid of industrial research.

Manchester, the metropolis of the world's cotton industry, has for many years also been the chief centre for the manufacture of dye-stuffs in this country, three of the principal English works being situated within the area of the city. Being so closely connected with the dye-stuff industry it is therefore remarkable that Manchester has not hitherto set about the task of specially training young men—or women—to undertake the research work without which the industry cannot attain pre-eminence. While Manchester University has always occupied a high place as a school of pure organic chemistry, and while the School of Technology has for years past done valuable work in teaching and investigating the application of dye-stuffs, it has fallen to the sister University of Leeds to build up, under the direction of Prof. Arthur G. Green, F.R.S., a school of colour chemistry of international reputation and importance. Here for a succession of years researches of fundamental importance for the dye-stuff industry have been carried out and published by Prof. Green and his students; it is sufficient to recall their researches on the stilbene dye-stuffs, on the quinonoid theory of colour, on the phthaleins, on the constitution of aniline black, and on the analysis of dye-stuffs to show what they have done.

Realising the importance of the dye-stuff industry to the country at large, and especially to the cotton area of which Manchester is the centre, the School of Technology (Faculty of Technology in the University of Manchester) has invited Prof. Green to take charge of a new department for advanced study and research in the subject of Coal-Tar Chemistry in the School of Technology. This department will be open only to post-graduate students or to those of equivalent attainments, whether trained in Manchester University (either in the School of Technology or in Owens College) or in other chemical schools of the country. The realisation of this scheme has been greatly assisted by the support rendered by the Privy Council Committee for Industrial Research.

Among those who will assist Prof. Green with the Research Department are Mr. F. M. Rowe, formerly one of his research assistants at Leeds, who has since studied under Freundlich at Brunswick, and Dr. G. Grant Hepburn, who was for some time research assistant to Noelting at Mulhouse and was afterwards chief chemist to a dyeing and calico printing works in Russia. Mr. Rowe obtained his M.Sc. degree by research on colouring matters at Leeds, and has recently been appointed Lecturer on Dye-stuffs in the University of Manchester. Dr. Hepburn obtained his Doctor's degree for chemical research in the University of Basle.

This pioneer staff will further have the valuable help and advice of Dr. Edmund Knecht, the Professor of Chemical Technology, who is well known as an expert in dyeing chemistry, on which he has published many researches.

The new laboratories were opened this week in the School of Technology. They have been equipped with special regard to the technical character of the work in question and provided with mechanical stirring and other appliances suitable for dealing with manufacturing processes. A library of special books and patent literature will also be installed.

It is confidently anticipated that the new department, with its strong teaching and research staff, will not only occupy the position of an important training centre for the young chemists required by our growing organic chemical industries, but will at the same time become a central research station for the chemistry of dye-stuffs and allied branches of applied chemistry. In this way it should render valuable assistance to this country by helping to build up afresh those industries in which for a time Britain has been outstripped by German enterprise and science.

Memorial to the late Sir William Ramsay.—A meeting to consider the steps to be taken to raise a memorial to the late Professor Sir William Ramsay, K.C.B., F.R.S., will be held at University College, London, on Tuesday, October 31, 1916, at 4.30 p.m. Invitations will be sent out on or about October 20. It will, however, greatly help in making the arrangements if all persons wishing to be present, including, in particular, scientific friends and former students of Sir William Ramsay, will send a postcard to the Secretary, University College, London, intimating their desire. Those who thus apply will not be asked to reply to the invitation when issued. Further particulars of the arrangements for the meeting will be issued in a few days. After the meeting the Director of the University College Chemical Laboratories, Professor J. Norman Collie, F.R.S., will deliver a memorial lecture on "The Scientific Work of Sir William Ramsay," at 5.30 p.m.

NOTICES OF BOOKS.

Report of the Committee of the Privy Council for Scientific and Industrial Research for the Year 1915-16. London: Wyman and Sons, Ltd. 1916. Pp. 56. Price 3d.

The report of the Advisory Committee of the Privy Council for Scientific and Industrial Research has been eagerly awaited by many different classes of people interested in education, in commerce, in research work, and other branches of scientific activity, and it was hoped that schemes for the solution of the problem of the organisation of industrial research would be outlined and possibly described in some detail. From this point of view the report is undoubtedly disappointing, for while summarising excellently the questions which require special consideration it lacks definiteness in its recommendations. It is shown how lamentably research has been starved in England, with a consequent decline or stunting of the growth of scientific industries, and the Government scheme aimed at remedying the defects of our present system is shortly discussed. The Committee at the outset decided to give science in its application to industry precedence over pure science, and conferences with professional societies were held, and registers of researches were made, with the result that grants were given to some forty individuals who were employed on important researches. Many standing committees were appointed, and their number will probably have to be added to in the near future. Besides describing the actual steps that have been taken the report discusses the attitude of manufacturers towards scientific research, and makes tentative and rather indefinite suggestions as to the betterment of that attitude. The need for a new outlook is emphasised, and the questions of the part the universities can play in the application of science to industry and the need for new institutes devoted to research only are discussed in general terms. The conditions necessary for the successful attainment of the aims of the Committee are summarised as being, firstly, a largely increased supply of competent researchers, and, secondly, a hearty spirit of co-operation between men of science, business men, working men, the universities and technical colleges, local authorities, and Government departments. With regard to the first condition it seems by no means improbable that there would be no lack of suitable workers if the outlook for the student who intended to devote himself to scientific research was from a material point of view no less promising and secure than that of his fellow-student who hoped to graduate in, say, medicine, and the question of the need for co-operation would appear to be intimately connected with that of educating the manufacturer and the working man, and, above all, our legislators as to the value of scientific methods, the importance of research, and the defects and dangers of our present systems.

Organic Agricultural Chemistry. By Joseph Scudder Chamberlain, Ph.D. New York: The Macmillan Co. 1916. Pp. xvii.+319. Price 7s. net.

Although this book has many good features and will be of real utility to agricultural students, to a certain extent it must be regarded as having fallen between two stools. It is from a scientific point of view decidedly above the head of the practical agriculturalist, who would find that it is too full of detail and expects too much of him in the way of previous knowledge, while the author fully recognises that it cannot meet the requirements of the student who wishes to become an agricultural chemist or other scientific worker in agriculture. Nevertheless, as far as the material is concerned the book will be found a satisfactory text-book dealing with the chemistry of plants and animals. The first part is devoted to systematic organic chemistry, and in it the author, assuming a knowledge of inorganic chemistry, describes the preparation and properties of the more important organic compounds found in plants and animals. A certain amount of illustrative practical work is described, and a good foundation is laid for the understanding of the second part, which is mainly physiological. A chapter on enzymes and their action gives a very good *résumé* of what is known on the subject. Animal food and nutrition are treated before plant physiology, the author believing that this order gives the student a correct view of plants and animals as living organisms. The third section deals shortly with crops, foods, and feeding, and discusses the occurrence and uses of the important constituents in plants, the food values of different feeding-stuffs, and the food requirements of animals.

Guide to Experiments for 1916. By Prof. Douglas A. Gilchrist, M.Sc. Newcastle-upon-Tyne: R. Ward and Sons. Pp. 91.

This pamphlet contains an account of the general character of the work done at the County of Northumberland Agricultural Experimental Station at Cockle Park, with details of the various trials of oats, barley, wheat, beans, &c., which have been carried out there. The manuring experiments which have been performed are described in full, and the valuable conclusions which may be drawn are summarised. These include important results relating to different phosphatic manures, obtained from tests extending over periods of from three to eight years, and the summaries of the results of the rotation experiments bring some interest facts to light. The accounts of the feeding experiments are published in separate bulletins.

Scientific Papers of the Bureau of Standards. No. 282. *Sensitivity and Magnetic Shielding Tests of a Thomson Galvanometer for Use in Radiometry*. By W. W. Coblentz. Washington: Government Printing Office. 1916. Pp. 24.

This report describes a series of experiments made to investigate the possibility of improving the sensitivity of galvanometers for use in radiometry. Galvanometer coils of various designs were first tested, and the paper describes the coil which was found to be most efficient. Also various astatic magnet systems were compared, and methods of shielding against magnetic disturbances were investigated. It was found that by mounting the coils in cavities in blocks of Swedish iron the effect of external magnetic perturbations could easily be reduced to one two-thousandth of its original value. A vacuum galvanometer gave the author a means of attaining a sensitivity ten times that reached in his earlier work on stellar radiation. The bulletin contains full experimental details of all the work that was done in the course of the investigation, and the results obtained were of the highest importance. A copy of the bulletin may be had gratis by sending a request to the Bureau of Standards, Washington.

Instruments for Recording Carbon Dioxide in Flue Gases. By J. F. Barkley and S. B. Flagg. Washington: Government Printing Office. 1916. Pp. 60. Price 10 cents.

Much interest has been taken recently in the question of the proper combustion of coal, and this has led to considerable activity in the devising of new forms of apparatus for analysing flue gases, especially for the determination of the percentage of carbon dioxide present. This bulletin describes a systematic series of tests of different instruments for the purpose, the investigation extending to the determination of their accuracy, the factors affecting their operation, the repairs and renewals necessary and their cost, &c. In all seven different kinds of instruments were examined, two being British made—the bimeter CO_2 recorder, made by the Cambridge Scientific Instrument Co., and the CO_2 thermoscope, made by the Underfeed Stoker Co., of London—while the others were American, German, or Swiss, and results and conclusions are very carefully and fully stated for each different kind of instrument.

The data collected will be of considerable practical value, for the tests of which accounts have been previously published have usually been made upon a laboratory scale only, whereas in this series of experiments the results which may be expected in ordinary practice were ascertained.

Circular of the Bureau of Standards. No. 56. *Standards for Electric Service.* Washington: Government Printing Office. 1916.

THIS circular of the Bureau of Standards contains suggested regulating ordinances for electric service in cities and towns, and also brief descriptions of the electrical testing equipment for the calibration and standardisation of "working test standards" used by central stations in their meter work and for making tests of consumers' meters. The bulletin may be obtained free upon addressing a request to the Bureau of Standards, and it will be found useful by electrical engineers, particularly in the United States.

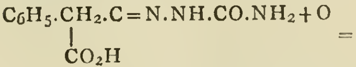
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 9, August 28, 1916.

This number contains no chemical matter.

No. 10, September 4, 1916.

Preparation of Acylsemicarbazides starting from Semicarbazones of α-Ketonic Acids.—J. Bougault.—When the semicarbazones of certain α-ketonic acids are oxidised by iodine and sodium carbonate they give the semicarbazides of acids containing one carbon less than the original acid. Thus the semicarbazone of phenyl pyruvic acid gives the semicarbazide of phenyl acetic acid. The reaction is—



$$C_6H_5.CH_2.\underset{\displaystyle CO_2H}{\underset{|}{C}}=N.NH.CO.NH_2+O=$$

$$=CO_2+C_6H_5.CH_2CO.NH.NH.CO.NH_2.$$

The reaction takes place very easily and in the cold. It is only necessary to dissolve the semicarbazone in a little water containing an excess of sodium carbonate and then add iodine (I+KI). The acylsemicarbazide is immediately precipitated, and may be purified by dissolving in water acidified with HCl, filtering, and precipitating by saturation with sodium carbonate. By this method the author has prepared three new semicarbazides.

MISCELLANEOUS.

Industrial Chemistry and Dyeing as a Career for Men and Women.—The prospectus of the chemistry and dyeing department of the Bradford Technical College contains detailed information of the courses arranged for training in these subjects. The time-tables given show that the diploma course provides a very thorough and well-balanced training in chemistry and physics and some of their applications, and much time appears to be devoted in the later years of the course to work in the practical dye-house, and to technical analysis, for those who are specialising in dyeing, while the other chemical industries are equally fully treated for the benefit of those students who intend to devote themselves to work in oil and soap manufacture, metallurgy, &c. The Technical College provides courses for Managers, Industrial Chemists, Dyers, Metallurgical Chemists and Assayers, Gas Engineers, Textile Chemists, Chemical Engineers, and other technical positions in the British chemical industries, and a separate pamphlet is issued dealing with Pharmacy and Dispensing as a profession for women.

TO comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged in Government work will be engaged."

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THE CHEMICAL NEWS

Vol. CXIV., No. 2970.

ON THE

X-RAYS AND THE THEORY OF RADIATION.[*]

By C. G. BARKLA, F.R.S.,
Professor of Natural Philosophy in the University of Edinburgh.

(Abstract).

The processes of emission of X-rays may be considered under three heads, the names we apply to the radiations produced:—(1) Scattered X-radiation, (2) Fluorescent (characteristic) X-radiation, and (3) Primary X-radiation.

Scattered X-Radiation.

Experiments on the quality, polarisation, distribution, and the intensity of the scattered radiation from any given substance, show that it is a radiation emitted by electrons whose motion—that part resulting in radiation—is very completely controlled by the primary radiation.

The fact that the simple theory shows that—

1 atom of H contains 1 electron
C ,, 6 electrons
N ,, 7 ,,
O ,, 8 ,,
S ,, 16 ,,

with very slight variation, is most remarkable evidence as to the adequacy of an unmodified theory of electromagnetic radiation. (The conclusions regarding the atom have been confirmed and are becoming generally accepted).

These results admit of no possible explanation but that every electron in the radiating matter is disturbed by every wave of the primary radiation; that radiation is a continuous process, not dependent on any limiting condition; that it may take place in any quantity.

There is not only no suggestion of a quantum or entity of radiation, but the phenomena become absolutely meaningless on any such theory.

Recent experiments have shown fairly conclusively that scattering takes place by groups of electrons rather than by individual electrons, when the wave-length is comparable to the size of a group.

Fluorescent (Characteristic) X-Radiation.

In contrast with the scattered radiation, the quality of the characteristic X-radiation, the absence of all polarisation effects, the uniform distribution, and the variation of intensity with wave-length of the exciting primary radiation show that the process of radiation is absolutely uncontrolled by the primary radiation exciting it. The emission of this radiation is conditional upon the primary beam being of shorter wave-length (an extension of Stokes' Law).

It is not an immediate result of the passage of the primary beam, but arises only indirectly from it, and it takes place only as an accompaniment of an exceptional disturbance of a radiating atom. It is natural to look to the ejection of a high-speed electron as this disturbance.

The character of the radiation and the intensity are independent of the speed of ejection or the career of an electron after ejection from the parent substance. The radiation therefore does not originate outside the parent atom, nor does it originate in this electron at all, for this is previously under the influence of the primary radiation. We are thus led to look for the origin of the radiation in an atom from which an electron has been expelled.

A study of the relation between a fluorescent X-radiation, the corpuscular radiation, and the absorption of the primary beam accompanying it, throws a great deal of light on the process.

Absorption—The emission of a fluorescent characteristic) X-radiation is accompanied by a special absorption of the primary exciting radiation, which can readily be distinguished. Thus if S is the energy of primary radiation re-emitted as scattered radiation, E_K, E_L, &c., are the energies absorbed in association with the emission of fluorescent radiations of series K, L, &c., respectively.

$$\text{Total energy absorbed } E = S + E_{M,N\ldots} + E_L + E_K + E_J.$$

Corpuscular Radiation.—Similarly the total corpuscular radiation may be divided into different groups, each group being definitely associated with the emission of a particular radiation. Thus—

$$C = C_{M,N\ldots} + C_L + C_K + C_J.$$

Careful experiments on the K absorption, K corpuscular radiation, and K fluorescent X-radiation from bromine lead to the following approximate conclusions:—

(1) The energy of primary radiation required to expel a K electron is greater than that per L electron by the energy of a quantum of K characteristic radiation. The energy of a quantum of K radiation is therefore the energy required to move an electron from the position and state of a K electron to the position and state of an L electron (for more precise statement, see *Phil. Trans.* paper).

(2) The energy of primary X-radiation absorbed by each atom from which an electron is expelled varies from just less than two quanta of primary radiation to just more than one quantum, as the wave-length of the primary radiation diminishes.

Thus absorption is not in quanta, or indivisible units.

(3) One quantum of K fluorescent characteristic radiation is emitted for each K electron ejected. (Experiments indicate that this emission is subsequent to the ejection of the electron).

Though there is evidence that with other substances these results do not hold so accurately, the general phenomena and the orders of magnitude are the same. It must therefore be concluded that these express the fundamental facts in outline at least. Modifications there will probably be; indeed, theory suggests that these may be necessary, but experimental evidence of sufficient accuracy has not yet been obtained to justify their inclusion as a statement of fact.

(The results indicate, too, that the energy of X-radiations of differing wave-length may be compared with fair accuracy, at least, by measurements of the total ionising power).

Theory of Radiation. — These experimental results suggest that characteristic radiation (say, K series) is emitted when an outer electron drops into the position of a displaced K electron, the energy previously absorbed in displacing the K electron, in excess of that carried away as kinetic energy, being now re-emitted as a quantum of K radiation, or more probably as a quantum of each of the K, L, M, radiations. The various lines in each series may be accounted for.

A New Series of Characteristic Radiations (J Series).—For many years there have been indications of radiations emitted by light elements not falling within the two series K and L. An apparent deviation of the experimental results from what was expected on the above theory led to the discovery of a new series of fluorescent radiations emitted by carbon, nitrogen, aluminium, and sulphur. From nitrogen the absorbability $(\lambda/\rho)_{Al}$ is about 2·5; from aluminium the radiation is more penetrating, and from sulphur more penetrating still. The series thus possesses similar characteristics to the lower frequency series.

Primary X-Radiation.

As the generation of a radiation of given penetrating power or frequency by cathode rays necessitates the incidence of electrons with energy greater than that of a quantum of that radiation even for the production of radiation not recognisable as characteristic of the anticathode, it seems probable that the process of generation of X-rays is one of the same character as that resulting in the emission of characteristic radiation. It is doubtful if mere collisions produce the radiation recognised as X-radiation. There is no conclusive evidence, however, of a limit to the wave-length of the X-radiation which may be generated in any particular anti-cathode.

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[*] The Bakerian Lecture, delivered before the Royal Society, May 25, 1916.

The Quantum-Theory.

Thus though X-radiation may be and is *emitted* by electrons (probably by groups of electrons or even atoms) as a continuous process and in any quantity whatever, it is emitted in quanta from atoms when certain critical conditions are reached.

X-radiation is *absorbed* in very minute quantities—very small in comparison with a quantum—in certain processes. In other processes it is absorbed only in quantities greater than a quantum of the primary radiation—quantities varying from one to two quanta. There is no evidence of absorption of X-radiation in whole quanta.

X-ray phenomena do not support the quantum theory of radiation as generally understood. They indicate that the quantum is a unit of atomic energy rather than of radiation; this unit necessarily appears in certain processes of radiation and absorption.

PRECISION IN CHEMICAL WEIGHING.

By WILLIAM NORMAN RAE and JOSEPH REILLY.

(Concluded from p. 189).

In most chemical work we are only concerned with relative weights, and therefore any inequalities in the lengths of the two arms of the beam are of no importance. When necessary the ratio of the lengths of the arms can be obtained, and also, assuming that the weights are accurate, the true weight of the body, by using Gauss's method. The body is first weighed in the left pan (apparent weight say X) and then in the right pan (apparent weight say Y); then, if L and R are the lengths of the arms and M the true weight of the body, by taking moments about the centre of the beam in the two cases—

$$\begin{aligned} & & M \times L &= X \times R \\ &\text{and} & Y \times L &= M \times R, \\ &\text{from which} & L/R &= X/Y, \\ &\text{and} & M^2 &= xy \\ & & M &= \sqrt{xy}. \end{aligned}$$

In general no appreciable error is caused by taking—

$$M = \frac{X+Y}{2}$$

The value of L/R on a good balance is usually very near to 1; the actual value in the case of an Oertling balance used by one of us is 1·00003. The value of the ratio can be altered by shifting the position of one of the knife-edges by means of the screws provided. It should be emphasised that such adjustments should only be made by a good instrument maker. The effect of even a very small alteration in the distance causes a big error in the weighing. The difference of the apparent weight in the two scale pans is the reason for always placing the object to be weighed in the left pan. Another method of obtaining the true weight of a body is by using two sets of weights, A and B, in the following manner:—Place the object on the left pan and balance it with the weights A, remove the object from the left pan and replace it by the weights B until balance is again obtained: the object and the weights B have now been balanced against the weights A under identical conditions, and the object therefore has a mass equal to that of the weights B used. The method of standardising weights as given by Sir William Crookes (*Proc. Royal Soc.*, 1872) we have found to work quite satisfactorily (see Chem. News, April 19, 1867, for complete details).

The above methods of weighing are sufficiently accurate for all ordinary laboratory work, but when greater accuracy is required greater precautions must be taken. Probably the disturbing effects of temperature are the cause of most of the difficulties. In the first place, inequalities of temperature will cause convection currents, which may make it difficult to get a constant zero, or by acting on one arm of the beam more than the other may cause an object to appear heavier or lighter than it really is. In the second place, a change of temperature will alter the lengths of the two arms of the balance, and although these are constructed of the same material their expansion coefficients may not be quite the same. One effect of this is the change in the zero which takes place throughout the day; this has been observed by many workers. Poynting noticed it in the case of an Oertling vacuum balance which was covered with felt and then with well polished tin, leaving only a small window for the observation of the pointer. The change was found to follow the temperature of the balance-room. The same trouble was encountered in his experiments on the determination of the mean density of the earth. We have carried out some experiments in which the balance was first used in a room in which most of the radiation fell on the side. Observations on the unloaded balance showed that the zero shifted an amount corresponding to an apparent weight change of 0·2 mgrm. between 9 a.m. and 3 p.m., while the temperature of the balance room was rising, and when the latter began to fall the zero started to creep back, but on the next morning it had quite recovered. The balance was then turned through an angle of 180°, and after leaving twenty-four hours to settle down the observations were repeated with the same results. The position of the zero again rising from scale division 10 to 12 in the morning, and commencing to fall towards the evening, although the radiation now fell chiefly on the opposite side. The same result is obtained with the pans loaded. The result of a change in the ratio of the arms can be found for different temperatures and an allowance made for it when weighings are made of the same object at slightly different temperatures. This source of trouble is much aggravated by large changes of temperature, and shows the importance of a steady temperature in the balance room and of reading the temperature of the balance case each time a weighing is made or the zero determined.

Besides this gradual change of the zero a temporary change may be produced by the unequal heating of the beam by the operator's hand in loading the balance. This point has been very thoroughly investigated by Manley (*Phil. Trans.*, A, ccx., 407), who found that a great improvement in this respect was brought about by enclosing the beam in a protecting case within the ordinary case. Manley showed that within an ordinary balance case when the balance is in use that there is a constant fluctuation in temperature to the extent of 0·2° C. in the neighbourhood of the beam. Adopting a protecting case uniformity in the temperature of the enclosed balance beam is obtained. The covering acts in addition as a dust-proof case. Landolt was also well aware of the disturbances caused by slight temperature changes in the balance case, and in his experiments on the constancy of mass in chemical reactions took his readings and also loaded the balance and interchanged the contents of the pans from a distance of three metres. In addition most of his weighings were taken at a standard temperature, approximately 19°, applying a small correction calculated from the known temperature coefficient of his balance when the temperature at the time of weighing deviated from 19°. It is instructive for a person to try a few experiments with a sensitive balance, weighing the same object repeatedly and consecutively without altering the balance, and also to weigh the same object at different times of the day. The effect of altering the position of the worker in weighing could also be noticed. In the above cases it is quite usual to get quite appreciable variations.

If the balance is loaded and the beam released so as to swing with a large amplitude, readings can be taken of the turning-points until the pointer practically comes to rest and the R.P. can be calculated for various amplitudes. It is always advisable to neglect the first few swings, when the beam may be supposed to be in a disturbed state due to the three knife-edges not being released at exactly the same instant. Irregular values of the R.P. are found with large amplitudes, but the value tends to become steady when the amplitudes do not exceed five divisions. Manley ascribes this to a slight lateral shift of the knife-edges, which is more pronounced unless the latter are attached by the method mentioned above.

When obtaining the weight of a substance very accurately the following procedure should be followed:—The pointer is observed through a reading telescope two or three metres away from the front of the case. This enables the observer to estimate to a tenth of a scale division with fair accuracy, avoids errors due to parallax, and prevents the parts of the balance being unequally heated by radiation from the observer's person. If artificial illumination is used it should be from directly behind and above the observer. The balance case is often covered with a non-conducting jacket, leaving only a small aperture for the observance of the scale. The pans are dusted with a camel-hair brush kept for that purpose, the case is closed and the beam released and left to swing for twenty minutes to become thoroughly fatigued. This avoids small errors due to slight changes in the positions of the small adjusting screws on the beam. If the amplitude is then too small for observations to be made conveniently it is increased, and after a few preliminary swings the turning-points are recorded for five or seven swings, and from these the zero is calculated. The temperature of the case is read and the barometric height is recorded.

The object to be weighed is then removed from the desiccator, wiped with a piece of silk, placed on the left-hand pan and balanced with weights. The case is then closed and left for some hours. The beam is then released and left to swing for twenty minutes in order for it to become properly fatigued, and the R.P. is determined. The weights used should be such as to give a R.P. just greater than the zero; 1 mgrm. is added by means of the rider and the new R.P. is determined. The difference between the two values gives the sensitiveness; the temperature and barometric height are recorded. The object and the weights are then interchanged, and after waiting some time (a shorter time than in the first case is sufficient) the beam is released, fatigued for the usual time, and the R.P. determined; 1 mgrm. is added, and from the new R.P. the sensitiveness is determined. Temperature and pressure are again recorded. Finally, after the object is removed, the zero is again determined and the temperature read. If the two values or the zero differ, owing to the temperature having altered, the value at each of the temperatures at which weighings were made is calculated, and these values of the zero are used in conjunction with the R.P.'s and sensitiveness already found, to calculate the apparent weight in each pan. The two weights so obtained are corrected for errors in the weights themselves and are corrected to vacuum in the manner presently to be described; the arithmetic mean of these two weights is taken to be the true weight of the body. The time allowed for the body to remain in the case before the weighing is commenced will depend on the size and nature of the object, as has already been mentioned. In some cases better results are obtainable by balancing the object with a similar tare, and in other respects proceeding as above. Noyes in the determination of the atomic weight of hydrogen had occasion to weigh glass vessels containing the reagents under experiment. Before placing in the balance case the vessels were always wetted and then wiped dry with a clean cloth; they were then placed in the balance pan and balanced with a piece of glass apparatus of the same size and weight (in the case of hydrogen the difference of volume between the object and its tare was 0·3 cc. and in weight 2 grms.) and small weights. A stream of dried and filtered air was then passed through the case for from twelve to twenty-four hours. The air current was stopped about twenty minutes before the weighing was made. After weighing, the air current was again started and the weighing repeated after an hour. The average difference between the two weights was 0·05 mgrm., while vacuum corrections had only to be applied to the weights used and for the small difference in the volume of the object and its tare. Advantage is often taken of the absence of vibration due to trains, trams, and machinery at night and the weighings are then made.

Landolt estimates that the degree of accuracy attainable is 0·03 mgrm., while Manley places it at 0·006 mgrm. The authors are of the opinion that the former figure is rarely attained in practice. In all cases it should be remembered that extreme accuracy in the weighing is of no value unless all the other operations involved can be carried out with accuracy of the same order; in fact, it is only in research work that any attempt to obtain accuracy to more than 0·1 mgrm. is necessary or desirable.

The Assay Balance.—These balances have a maximum load of about 2 grms., and are sometimes sensitive to 0·01 mgrm. They can therefore be used very conveniently for accurate determinations of small weights. The same principles are used in the construction of these balances as in those for heavier loads, but, since the loads are to be small, increased sensitiveness can be secured by making the parts light as far as is consistent with rigidity. Both short and long beam assay balances are made.

Micro Balances.—These instruments are intended for the determination of weights of the order of a few mgrms. only. The ordinary Nernst form is sensitive to 0·001 mgrm., while Steel and Grant describe one instrument for weighing 0·2 grm. to 0·0001 mgrm. and another for detecting changes of weight of the order of 0·000004 mgrm.

Nernst's micro-balance has a bent glass capillary tube for beam; this tube is about 30 cm. long and 0·05 cm. in diameter; it is cemented at a point one-third of its length from one end to a fine quartz thread stretched between two metal prongs. It is therefore a torsion balance; the long arm is bent down at right angles and then outwards, and terminates in a fine point which moves over a graduated scale. The pointer is bent outwards at such an angle that if produced back it would pass through the point of suspension. The short arm has a platinum hook fused on, and this carries a small platinum scale pan about 1 cm. in diameter. The weight of the scale pan is balanced by a platinum rider cemented on to the other arm. The beam is raised from the arrestment in the usual way by a cam and thumbscrew. The scale can be calibrated with known weights and small objects can be weighed by substitution. The maximum load is 2 mgrms.

In the instruments described by Steel and Grant the principle involved in weighing is as follows:—A small quantity of air (0·01 mgrm.) is sealed in a quartz bulb; if the balance case contains air of the same density as the enclosed air (*i.e.*, air at the same temperature and pressure) the apparent weight of the enclosed air will be zero, while if the pressure in the balance case be zero the apparent weight of the enclosed air will be 0·01 mgrm.; the pressure can be read to one-tenth of a mm., and can be varied from 0 to 760 mm., so that the apparent weight of the enclosed air can be varied by $\frac{1}{10} \times 0{\cdot}01 \div 760$ mgrm.; *i.e.*, $1{\cdot}3 \times 10^{-6}$ mgrm. This reasoning assumes that the beam of the instrument is homogeneous and that the zero remains constant, conditions which are found to be obtainable. The balance is made entirely of quartz, since this material combines lightness with strength, does not corrode, has a small temperature coefficient, and is only slightly hygroscopic; it can also be obtained in a pure condition and can be readily cleaned. The beam consists of a framework of quartz rod and is about 5 cm. long, and carries two small quartz knife-edges about 1 cm. apart at its centre and also a small mirror. A fixed counterpoise is attached to one end of the beam, and to the other is fused a fine quartz fibre $\frac{1}{2}$ cm. long with a hook at its lower end to which is attached a short quartz rod, then a sealed-up quartz bulb, below this a quartz scale pan, and, lastly, one of a series of quartz counterpoises. In some form the scale pan, &c., are suspended by a knife-edge. The balance is contained in a small metal case with a plate-glass window in the end through which a beam of light can be thrown on the mirror and reflected back on to a scale.

The cover has a broad flange, ground to give an air tight joint when lubricated, with a corresponding flange on the base. The beam arrestment is worked by means of a cam actuated by a thumbscrew outside; the axis of the latter is ground conically to fit a tapering brass tube made air-tight by lubricating. To the side of the case is attached a manometer and a two-way tap for exhausting. In the base, by means of a ground glass joint, fits a glass tube in which hangs the scale pan, &c. In weighing the rest-point is first observed with no load on the pan and at some fixed pressure p; the weight of air in the quartz bulb is known from the volume of the bulb (determined by weighing it full of mercury), and the temperature and pressure of the air at the time of sealing it up. Suppose this pressure is P and the weight of air W; now with the load on the pan the pressure is adjusted to some value, p', which brings the beam to the same resting-point as at the first; the weight of the substance in the pan is then $\frac{W}{P}(p-p')$; *e.g.*, if the weight of air in the bulb was 0·01 mgrm. and the pressure at the time of sealing 750 mm., while the resting-point was the same with no load and a pressure of 640 mm., and with the load at a pressure of 42 mm. the load would be—

$$\frac{0{\cdot}01 \times (640-42)}{750};$$

i.e., 0·00797 mgrm.

To weigh larger quantities the counterpoise below the balance pan is replaced by a lighter one of known weight (determined on the micro balance itself), and the difference of the weights of the two counterpoises at the two pressures is added to the weight determined as above.

Vacuum Corrections.—When an object is weighed in air, both the object and the weights used, owing to the buoyancy of the air, lose weight equal to the weight of the volume of air displaced; since the weight of a given volume of air depends on the temperature, pressure, and humidity the buoyancy of the air varies and therefore the apparent weight of an object will also vary from day to day. To overcome this difficulty the apparent weight of the body is corrected to what it would be *in vacuo*. Suppose the body to have a mass m and a density ρ, while the density of the air at the temperature, pressure, and humidity at the time of weighing to be δ, the volume of the body is $\frac{m}{\rho}$ cc., and this is also the volume of air displaced; this air weighs $\frac{m\delta}{\rho}$ grms., and the real weight of the body *in vacuo* is therefore $\frac{m\delta}{\rho}$ greater than its weight in air. In the same way the weights used lose weight $\frac{m\delta}{\rho_1}$ where ρ_1 is the density of the material used in the construction of the weights; this makes the body appear lighter than it really is, so that a correction to the apparent weight must be made by adding $\frac{m\delta}{\rho} - \frac{m\delta}{\rho_1}$; the corrected weight *in vacuo* is therefore—

$$M = m\left(1 + \frac{\delta}{\rho} - \frac{\delta}{\rho_1}\right).$$

To get an idea of the magnitude of this correction we will consider the effect of a variation of 5° C. in the temperature and 1 cm. in the height of the barometer, on the weight of an object of density near to 1. Taking the density of air to be approximately 0·0012, a variation in the temperature of 5° will alter this by 1/60th, so that the change in the apparent weight of 1 cc. will be +0·00002 grm., while for 1 cm. change of pressure the apparent weight change will be 0·000016 grm.; should both changes occur so as to affect the weight in the same direction the change would be 0·000036 grm. per cc., so that in weighing to the fourth place this is not negligible for volumes of 2 cc. or more.

As already mentioned the value of δ will depend on the temperature, pressure, and humidity of the air in the balance case, and of these the humidity is not known with accuracy; Kuhn found it to be between 55 and 60. Wade and Merriman estimate it to be 50 per cent, and Brauner found it to be 35 per cent, so that the ordinary desiccating agents used give very variable results; the effect on the density of the air of a change of 10 per cent in the neighbourhood of a humidity of 60 per cent is 0·000001 grm. per cc.; *i.e.*, 0·1 mgrm. on 100 cc., and the value of δ is also required to four significant figures in the same case.

Many writers, *e.g.*, Kohlrausch, suggest the use of 0·0012 for δ; this is obviously of insufficient accuracy. In order to get the vacuum correction to 0·0001 grm. in the case of an object of density about 2 and volume 100 cc. we require the value of δ to 0·000001, and therefore to know the temperature, pressure and relative humidity to a close degree of accuracy.

T. to 0·5° per cent.
P „ 1 mm.
R.h. „ 10 per cent.

It will be seen that the correction $m\left(\frac{\delta}{\rho} - \frac{\delta}{\rho_1}\right)$ is zero when the object and the weights have the same density, and will have the greatest value when ρ and ρ_1 are widely different; *e.g.*, with brass weights and objects of density 1, 2, and 3, and taking $\delta = 0{\cdot}0012$ the value approximately of the correction will be:—

i. .. $m\delta(1-\frac{1}{8}) = \frac{7}{8}\,m\delta = 0{\cdot}001m.$
ii. .. $m\delta(\frac{1}{2}-\frac{1}{8}) = \frac{3}{8}\,m\delta = 0{\cdot}0005m.$
iii. .. $m\delta(\frac{1}{3}-\frac{1}{8}) = \frac{5}{24}\,m\delta = 0{\cdot}0002m.$

Owing to the uncertainty of the vacuum corrections it is advisable to make them as small as possible, especially when weighing objects of large volume; the use of tares in the latter case is almost universal, the only vacuum correction then required being for the difference in volume of the object and its tare, which difference is small.

With the same object, the use of quartz weights for weighing glass apparatus has been suggested; these are practically unchangeable in the air, but are easily broken if accidentally dropped, while their cost puts them beyond the reach of most laboratories.

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SENSITIVENESS TO DETONATION OF TRINITROTOLUENE AND TETRANITROMETHYLANILIN.*

By GUY B. TAYLOR and WILLARD C. COPE.

Introduction.

The tendency in the development of the modern blasting cap is toward partial replacement of the hitherto exclusively used mercury fulminate by other explosive substances. At present the practice is largely to superimpose a small charge of fulminate, its chlorate mixtures, or lead hydronitride, upon organic nitro compounds or nitrates in the detonator shell. The detonator is usually of the " reinforced " type, in which an inner perforated shell is pressed down over the charge. The sensitive fulminate composition, fired by fuse or electrically, detonates the secondary explosive, thereby transmitting the impulse that causes the blasting explosive to detonate.

This plan of superimposing an initial primer upon a secondary explosive in a detonator shell offers an excellent arrangement, not only for practically working out the best combination for commercial detonators, but for studying theoretically the process involved in the transmission of the detonating wave from the initial primer to a secondary explosive, and has been used by several investigators (see L. Wöhler and O. Matter, "Beitrag zur Wirkung der Initialzündung von Sprengstoffen," *Ztschr. ges. Schiess- u. Spreng-stoffw.*, 1907, Bd. ii., 181, 203, 244, 265; Martin, " Uber Azide und Fulminate," Darmstadt, 1913; C. G. Storm and W. C. Cope, " The Sand Test for Determining the Strength of Detonators," *Tech. Paper* 125, *Bureau of Mines*, 1916, pp. 1-64.

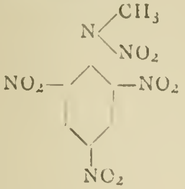
Usual Method of Performing Detonation Experiments.

The experiments are usually carried out by weighing into the copper shell a fixed quantity of explosive (trinitrotoluene, picric acid, gun-cotton, or the like) and varying the weight of primer until the minimum quantity required for certain detonation is ascertained. It is obvious that the method may be used either to compare the relative sensitiveness of explosives towards the same primer or the relative efficiencies of different priming compositions in detonating the same explosive.

Character of Explosives Used in Present Investigation.

In the present investigation, which was conducted in the Explosives Chemical Laboratory of the Bureau of Mines at Pittsburgh, the object was to study the action of initial primers.

Two explosives, varying fairly widely in sensitiveness to detonation, were selected for this work—namely, trinitrotoluene and trinitromethyl nitramine. Trinitrotoluene, symmetrical trinitromethylbenzene, $C_6H_2CH_3(NO_2)_3$, is known as an explosive under a variety of names—trotyl, trinol, trilite, tritolo, or T.N.T. The latter term is used in this paper. Trinitromethylnitramine has the structural formula—



and is generally known as tetranitromethylanilin (see R. Escales, " Die Explosivstoffe," 1915, Ht. 6, p. 368), or more simply tetryl. The latter term is used in this paper.

Sensitiveness of T.N.T. and of Tetryl as Determined by Other Investigators.

Will (" Zur Frage der Prüfung von Sprengstoffen auf Transportsichenheit," *Ztschr. ges. Schiess- u. Sprengstoffw.*, 1906, Bd. i., 209) has reported the relative sensitiveness to blow of a number of explosives. The height of drop necessary for a 2-kilogrm. weight to cause detonation of T.N.T. in an impact machine varied from 57 to 90 cm., depending on the physical condition of the explosive; for tetryl the height was 40 to 65 cm.

According to a report by the Rheinische Westfalische Sprengstoff A. G. (see A. J. Stuart, " Lead Hydronitride," translation, *U.S. Artillery Jour.*, 1914, xli., 212) the following minimum charges for detonation of 1 grm. of the nitro compounds in reinforced detonator shells 45 by 6·85 mm. were obtained.

Minimum Weight of Various Charges required for Certain Detonation of T.N.T. and of Tetryl.

Charge.		T.N.T.	Tetryl.
Mercury fulminate	Grms.	0·35	0·40
Mercury fulminate, 80 per cent.	,, }	0·30	0·20
Potassium chlorate, 20 ,,	,, }		
Lead hydronitride	,,	0·08	0·01

Martin (data obtained from A. Stettbaoher, " Altes und Neues über Initialzundstoffe," *Ztschr. ges. Schiess- u. Spreng-stoffw.*, 1914, Bd. ix., 355) has also determined the minimum charge of several primers required to detonate these two explosives. A loading pressure of 1100 kilogrms. per square cm. was used in the reinforced detonator. The results of Martin's determinations follow:—

Results of Martin's Determinations of Minimum Charges required to Detonate Nitro Compounds.

Charge.		T.N.T.	Tetryl.
Mercury fulminate	Grms.	0·36	0·29
Silver fulminate..	,,	0·095	0·02
Cadmium fulminate	,,	0·11	0·008
Mercurous hydronitride	,,	0·145	0·015
Silver hydronitride	,,	0·07	0·02
Lead hydronitride	,,	0·09	0·025
Cadmium hydronitride	,,	0·04	0·01

It will be noted that Martin's results show a wide range in the efficiency of various initial primers, but that tetryl was more sensitive than T.N.T. in every case.

According to Giua (" Die Industrie des Trinitroluols in Italien und deren Entwicklungsbedingungen," *Ztschr. ges. Schiess- u. Sprengstoffw.*, 1915, Bd. x, 109; " Miscugli di Explosivi Nitrati e Nitrazione del Toluene," *Gaz. Chim. Ital.*, t. 45, pt. 2, July 18, 1915, p. 32) tetryl when fused with T.N.T. makes the latter explosive more powerful and at the same time more sensitive. It is claimed that an addition compound is formed between the two, as shown by thermal analysis.

Authors' Method of Preparing Explosive Mixtures Tested.

In the authors' experiments the mixtures of tetryl and T.N.T. were made by fusing together the two substances and obtaining careful cooling curves. The cooling curves were obtained from different masses of melt and under

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* *Technical Paper* 145, *Bureau of Mines, U.S.A.*

TABLE A.—*Results of Sand Tests of* 0·4000 *grm. Mixtures of Trotyl and T.N.T., with varying weights of Fulminate-chlorate* (90 : 10) *Primer in reinforced Detonators.*

Explosive mixture.	Weight of primer, grms.								
	0·32.	0·25.	0·24.	0·23.	0·22.	0·21.	0·20.	0·19.	0·18.
	Weight of sand pulverised finer than 30-mesh, grms.								
100 per cent T.N.T. and 0 per cent. tetryl ..	37·5	34·4	—	--	—	—	—	—	—
	38·0	34·7	—	—	—	—	—	—	—
	37·6	34·1	(a) 13·2	(a) 13·9	—	—	—	—	—
	37·8	35·1	—	—	—	—	—	—	—
	37·3	33·8	—	—	—	—	—	—	—
	(b) 37·6								
90 per cent T.N.T. and 10 per cent tetryl.. ..	—	—	—	—	31·6	25·0	—	—	—
	—	—	—	—	30·1	—	—	—	—
	38·0	—	30·6	—	32·3	(a) 13·4	(a) 13·8	—	—
	—	—	—	—	27·8	—	--	—	—
	—	—	—	—	28·6	—	—	—	—
80 per cent T.N.T. and 20 per cent tetryl.. ..	—	—	—	—	—	27·0	—	—	—
	—	—	—	—	—	28·7	—	—	—
	39·0	—	—	—	34·1	32·3	(a) 11·2	—	—
	—	—	—	—	—	33·3	—	—	—
	—	—	—	—	—	32·0	--	—	—
50 per cent T.N.T. and 50 per cent tetryl.. ..	—	—	—	—	—	—	31·5	—	—
	—	—	—	—	—	—	29·4	29·2	—
	39·9	—	—	—	—	—	30·7	(a) 10·8	(a) 12·9
	—	—	—	—	—	—	27·5	—	—
	—	—	—	—	—	—	29·3	—	—
0 per cent T.N.T. and 100 per cent tetryl.. ..	—	—	—	—	—	—	—	34·9	—
	—	—	—	—	—	—	—	36·0	35·5
	(b) 41·5	39·7	—	—	—	—	39·1	33·4	33·5
	—	—	—	—	—	—	—	33·5	(a) 5·4
	—	—	—	—	—	—	—	32·5	—

(*a*) Incomplete detonation. (*b*) Average of five shots.

widely different rates of cooling, but the authors were unable to confirm Giua's conclusion that an unstable compound of three molecules of T.N.T. to two of tetryl is formed. The tendency of the melts to supercool was great, and the heat effects of the crystallisation were so small as to render methods of thermal analysis untrustworthy.

The T.N.T. used was an imported sample of high purity known in the Bureau of Mines Laboratory under the number M 1789. The tetryl (M 1849) was crystallised once from benzene and melted sharply at 129·2° C., uncorrected. Mixtures containing 10, 20, 40, and 50 per cent of tetryl were made by fusion in a water-bath, the solid resulting on cooling being ground in a mortar. The minimum charge of primer consisting of 90 parts of mercury fulminate and 10 parts of potassium chlorate necessary for complete detonation was determined for each mixture except that containing 40 per cent. tetryl.

Method of Using Sand Test.

The "sand test" as developed by Storm and Cope (*loc. cit.*) for the direct testing of detonators offers a most useful and convenient method for the laboratory study of priming compositions. In this test the detonator is buried in the centre of 100 grms. of "Ottawa standard sand" contained in a cylindrical chamber, approximately 15 cm. deep and 3·1 cm. in diameter, bored out of a steel block. The sand is practically pure quartz, passes entirely through a 20-mesh screen, and is held on a 30-mesh screen. The grains from different lots are of remarkably uniform size. After the detonator has been fired the sand is screened, and the quantity passing through a 30-mesh screen is regarded as a measure of the strength of the detonator. In a long series of tests Storm and Cope found that the result given by the "sand test" was a definite function of the weight of the charge and that the quantities of sand crushed by mercury fulminate and its chlorate mixtures was comparable to their relative efficiencies in causing complete detonation of nitro substitution compounds. The test is an accurate indication of the grade of commercial detonators, Most other direct tests, such as the lead-plate test, are not quantitative, or depend upon effects not easily or accurately measured.

Details of Experiments.

The tests with T.N.T., tetryl, and their mixtures were carried out as follows:—Exactly 0·4 grm. of the explosive was weighed into a copper shell 5 mm. in diameter and slightly pressed with a neatly fitting glass rod having a flat end. The primer, 90 per cent mercury fulminate and 10 per cent potassium chlorate, was placed on top, and the thin copper reinforcing cap (9 mm. long with 2·3 mm. perforation) was inserted and pressed down into the shell for one minute under a loading pressure of 200 atmospheres per square inch (206 kilogrms. per square cm.). A short piece of fuse was crimped into the shell and the detonator fired in the sand bomb. The results of the individual shots are given in Table A.

(To be continued).

New Products of Electrochemical Oxidation of Phenol.—Fr. Fichter and Emile Brunner.—When phenol is oxidised in a concentrated solution with a current of feeble intensity, hydroquinone, quinone, pyrocatechin, *p-p'*-biphenol, *o-p'*-biphenol, and *o*-oxyphenylic ether are formed. Many of the products of the reaction are found in the resinous residue, distilling it at a very high temperature, and soluble in alkalis, representing condensation products of phenol of high molecular weight. It may be shown that the two biphenols are only intermediate products, by electrolysing them in the same conditions; they then yield the dioxybenzenes or their quinonic derivatives *o-p'*-biphenol giving quinone and pyrocatechin, and *p-p'* biphenol only quinone.—*Bulletin Soc. Chim. de France* xix.-xx., No. 8.

SOME QUALITATIVE TESTS FOR GUM ARABIC AND ITS QUANTITATIVE DETERMINATION.*

By C. E. WATERS and J. B. TUTTLE.

Introduction.

The group of polysaccharides includes such diverse substances as the starches, cellulose, the dextrins, the true gums, and the plant mucilages. They possess in common the property of being decomposable hydrolytically into one or more sugars, usually pentoses or hexoses. By oxidation the acids corresponding to these sugars are formed, but the first step toward this reaction appears to be hydrolysis.

The true gums, of which gum arabic is typical, dissolve in cold water, yielding clear solutions which, though viscous and adhesive, can be filtered. The closely related and quite similar mucilages, such as gum tragacanth and cherry-tree gum, simply swell up and form more or less homogeneous suspensions that cannot be filtered. Perhaps most of the so-called gums are mixtures of one or more representatives of the above classes.

As might be expected from their chemical nature, the gums do not readily lend themselves to reactions of a definite qualitative or quantitative value. One of us learned how unsatisfactory some of the qualitative tests are when samples of mucilage first came to the Bureau of Standards for examination. This led to an extended study of the literature and of the various qualitative reactions that have been published, and finally to a comparatively accurate quantitative method. In the last part of this work the two of us joined forces, hoping to carry on a much more extended investigation than was found later to be possible.

The object of this paper is to discuss briefly some of the more important qualitative and quantitative methods, and give references showing, as far as possible, what other methods have been published.

Qualitative Tests.

In nearly all cases a 2 per cent solution of gum arabic was used. Similar solutions of dextrin and of gum ghatti, a substitute for arabic, were subjected to the same tests.

1. *Ferric Chloride and Alcohol.*—A mixture of 2·5 volumes of 50 per cent alcohol and 1 volume of neutral ferric chloride solution containing 25 grms. of the salt in 100 cc., precipitates gum arabic, though often only on long standing (Roussin, *Journ. Pharm. Chim.*, 1868, [4], vii., 251; see also Allen's "Com Org. Anal.," 4th Ed., iii., 443). Gum ghatti gives no precipitate and dextrin a very slight one.

2. *Potassium Hydroxide.*—According to Liebermann (*Chem. Ztg.*, 1890, xiv., 665), solutions of gum arabic and of dextrin become amber-yellow when warmed with potassium hydroxide, while the closely related gum senegal gives at most a faint yellow colour. Sollman (*Am. Journ. Pharm.*, lxxxiii., 176; *Chem. Zentr.*, 1911, [1], lxxxii., 1560) stated that dextrin when so treated turns more or less brown, while some sugars and gums other than arabic behave similarly. Rideal and Youle came to the conclusion that this test is of no value (*Journ. Soc. Chem. Ind.*, 1891, x., 610). Two samples of gum arabic, among a number tested by them, gave a green colour; a solution of ghatti turned pink, and dextrin a very dark red or almost black. Nevertheless, this test is among those recommended in the latest edition of "Lunge" ("Chem.-Tech. Untersuchungsmeth.," 6th Ed., 1911, iii., 167). Our own experiments amply confirm the statements that this test is of no value.

3. *Colour Reactions with Phenols.*—Reiche found that gum arabic gives a flocculent blue precipitate when boiled with orcinol and concentrated hydrochloric acid (*Ber. Ges. Förder. Chem. Ind.*, 1879, 74; *Chem. Ztg.*, 1880, iv., 191). Other carbohydrates gave yellow or brown colours. Other investigators obtained reactions with other phenols (Ihl, *Chem. Ztg.*, 1885, ix., 231; Clermont and Chautard, *Comptes Rendus*, xciv., 1254; *Jahresber.*, 1882, 684). In our work, nine different phenolic compounds were used in alcoholic hydrochloric acid solution. Quite a wide range of colours was obtained, but the test was found to be unreliable for the carbohydrates which were studied.

4. *Basic Lead Acetate.*—An aqueous solution of neutral lead acetate precipitates neither dextrin nor gums arabic and ghatti. An alcoholic solution of the salt does, however, slowly precipitate gum arabic (Chauvin, *Mon. Sci.*, 1911, [5], i., 317; *Chem. Zentr.*, 1911, [1], lxxxii., 1656).

As might be expected from its employment in clarifying sugar solutions before polarisation, basic lead acetate is an excellent precipitant for many gums. The solution may be made basic by adding ammonia (v. Lippmann, "Chemie der Zuckerarten," 3rd Ed., p. 1616), or by boiling with litharge. The precipitate formed when gum arabic solution is added, is of a peculiar curdy consistency, and of such characteristic appearance that it is hardly necessary to make any confirmatory tests. Allen (*op. cit.*, p. 441) speaks of this precipitate as a "white jelly." Dextrin solutions are, at most, made slightly cloudy by the reagent, while gum ghatti yields a very small amount of precipitate, most of which remains suspended in the liquid.

The basic acetate solution used in this work was made by long continued boiling of 40 grms. of crystallised lead acetate, dissolved in 250 cc. of water, with an excess of litharge. It was filtered, after which it remained clear for a long time.

Basic lead acetate has been recommended probably more frequently than any other reagent as a qualitative test for gum arabic, as well as for removing this and other gums from wines, liqueurs, &c., in which other constituents are to be determined (Rideal and Youle, *Journ. Soc. Chem. Ind.*, 1891, x., 610; Fromm, *Zeit. Anal. Chem.*, 1901, xl., 143; Papasogli, *L'Orosi*, 1898, xxi., 263; Scheibler, *Zeit. Ver. Zuckerrind.*, xxiii., 288; Battut, *Sucr. Indig. et Colon.*, xxxii., 285; v. Lippmann, "Chemie der Zuckerarten," p. 1616).

5. *Copper Sulphate and Sodium Hydroxide.*—Jettel ("Zündwaren" in Lunge's "Chem. Tech. Untersuchungsmeth.," 6th Ed., iii., 167) does not mention the basic lead acetate test, but relies chiefly upon the behaviour of dextrin, gum arabic, &c., towards copper sulphate and sodium hydroxide. The test was devised by Liebermann for detecting dextrin and gum senegal in the presence of gum arabic (*Chem. Ztg.*, 1890, xiv., 635). The details are given quite fully by Jettel. We need only say that gum arabic gave a blue precipitate, the supernatant liquid being colourless. Ghatti gives a dark blue solution which is sometimes turbid, but which clears up on warming gently; there is a little reduction on boiling. Dextrin gives a precipitate which dissolves on warming; at the same time there is considerable reduction to cuprous oxide.

6. *Miscellaneous Qualitative Tests.*—Many other reagents for gum arabic have been suggested, but they need only be referred to as follows:—

(*a*) Oxidase reaction for distinguishing between gums arabic and tragacanth (Payet, *Apoth. Ztg.*, xxv., 116; *Zeit. Anal. Chem.*, 1905, xliv., 453).

(*b*) Warming with hydrofluoric acid as a test for gum arabic, glue, and dextrin (Bornträger, *Oesterr. Chem Ztg.*, 1888, iii.; *Zeit. Anal. Chem.*, 1901, xl., 131).

(*c*) Colour reaction with alkali and diazobenzene sulphonic acid (Petri, *Zeit. Physiol. Chem.*, viii., 291 *Jahresber.*, 1884, 1328).

(*d*) Reaction with acidified egg albumen as a test for gum arabic and dextrin (Günsberg, *Journ. Prakt. Chem* lxxxviii., 239; *Zeit. Anal. Chem.*, 1863, ii., 218).

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* Published by permission of the Director of the Bureau of Standards. Copies of the complete paper, from which this is abridged, can be obtained by application to the Director, Bureau of Standards, Washington, D.C. From the *Journal of Industrial and Engineering Chemistry*, viii., No. 5.

TABLE I.—*Chief Qualitative Tests for Gums and Dextrins.*

Reagent.	Gum arabic.	Gum ghatti.	Gum gedda.	Dextrin.
Ferric chloride and alcohol.	Precipitate.	Nearly clear.	Slight precipitate.	Slightly cloudy.
Basic lead acetate.	Dense precipitate.	Cloudy.	Less precipitate than arabic.	Slightly cloudy.
Copper sulphate and sodium hydroxide, cold.	Blue precipitate, colourless solution.	Dark blue solution, often cloudy.	Light blue precipitate, dark blue solution.	Dark blue solution.
Copper sulphate and sodium hydroxide, boiled.	Precipitate darker, pale blue solution.	Slight reduction.	Precipitate darker.	Complete reduction.
Iodine solution.	No characteristic colour reactions.			Reddish purple solution.

(*e*) Nessler's reagent to detect gelatin in gum arabic solutions (Vamvakas, *Ann. Chim. Anal. Appl.*, 1907, xii., 12, 139; *Analyst*, 1907, xxxii., 193, 226).

(*f*) Reduction of mercuric acetate in the presence of sodium chloride (Hager, *Pharm. Centr.*, xviii., 313; *Zeit. Anal. Chem.*, 1878, xvii., 380).

(*g*) Reduction of molybdic acid (Hager, "Commentar zur ersten Deutschen Pharmakopöe," ii., 116; *cf.* Stohmann in "Muspratt," 4th Ed., 1891, iii., 1917).

(*h*) Colour reaction with cobalt nitrate and alkali (Papasogli, *L'Orosi*, 1898, xxi., 263).

(*i*) Colour reaction with colloidal gold solution (Zsigmondy, *Zeit. Anal. Chem.*, 1901, xl., 697).

Other reagents for gum arabic, such as sodium or potassium silicate, borax, or ammonium oxalate (Allen, *Op. cit.*, p. 411), would seem to depend largely upon the natural calcium content of the gum, though some of the reagents are said to cause gelatinisation. In our work numerous other reagents were tried, but even such promising ones as basic zinc salts and sodium zincate were found to be useless.

In Table I. is given a comparison of the more reliable reactions for the identification of dextrin, gums ghatti and gedda, and for gum arabic from different sources. Some of these samples were obtained after most of the work described above had been completed, and only the tests tabulated were applied. All samples of gum arabic behaved alike.

Quantitative Methods.

Since the chemical nature of the gums is such as to render most of the qualitative tests of at least doubtful value, it is not surprising that there are difficulties involved in their quantitative separation and determination. Some of the methods that have been proposed will be mentioned below, after which our own procedure will be described.

1. *Ferric Chloride and Calcium Carbonate.*—The details of this method, which was proposed by Roussin, are given by Allen (*Op. cit.*; also, Auguet, *Ann. Fals.*, ii., 136; *Chem. Abs.*, 1911, v., 538).

2. *Ferric Chloride and Sodium Carbonate.*—This method was employed by Landwehr (*Zeit. Physiol. Chem.*, 1884, ix., 164) for the determination of glycogen, and, incidentally, of gum arabic. In connection with this he determined the percentages of water held by ferric hydroxide when dried to constant weight at different temperatures.

3. *Lead Acetate.*—The use of this salt, dissolved in alcohol, was proposed by Chauvin (*Ann. Fals.*, v., 27; *Chem. Zentr.*, 1912, [1], lxxxiii., 756), and recommended by Rocques and Sellier (*Ann. Chim. Anal. Appl.*, 1911, xvi., 218; *Chem. Zentr.*, 1911, [2], lxxxii., 394). As far as we know, the basic salt has not been used quantitatively. Various formulæ have been ascribed to the precipitate, and it is not unlikely that it varies in composition (Riegal, *Arch. Pharm.*, [2], liv., 155; *Jahresber.*, 1847–8, i., 795; Battutt, *Sucr. Indig. et Colon.*, xxxii., 285; Scheibler, *Zeit. Ver. d. Zuckerind.*, xxiii., 288).

4. *Alcohol.*—Chauvin employed alcohol acidified with hydrochloric acid to precipitate gum. The acid is unnecessary, for strong alcohol has often been used to precipitate gum from plant extracts, wines, &c. (Diehl, *Pharm. Rundschau*, i. 31; *Zeit. Anal. Chem.*, 1883, xxii., 622; Madsen, *Pharm. Centr.*, xx., 144; *Zeit. Anal. Chem.*, 1883, xxii., 134).

5. *Miscellaneous Methods.*—Methods depending upon hydrolysis (v. Lippmann, *loc. cit.*), followed by estimation of hexoses or pentoses, and those by which the gum is oxidised to mucic acid (Kiliani, *Ber.*, 1882, xv., 34), are of no value because samples of gum from different sources yield different percentages of the products. Wide variations in the iodine absorption, acidity, and the amount of alkali taken up from alcoholic potash, are also found (Williams, CHEMICAL NEWS, lviii., 224; *Zeit. Anal. Chem.*, 1889, xxviii., 732).

6. *Copper Sulphate and Alkali.*—Madsen (*loc. cit.*) estimated the gum in liquorice juice (*Succus liquiritiae*) by throwing it out with strong alcohol, dissolving in water, and precipitating with copper sulphate and sodium carbonate. The gum is not identical with gum arabic, but for botanical reasons may well be quite similar to it.

During the course of our work, while still unaware of the work of Madsen, it was attempted to use the same reagents, together with alcohol, to precipitate gum arabic quantitatively. The filtrates were always cloudy. Slightly better, but still far too low, results were obtained when sodium hydroxide instead of carbonate was used, and having the combined solutions contain 60 per cent of alcohol. Since any excess of copper over the gum present would be thrown down as hydroxide, thus increasing the difficulty of washing and drying the precipitate, some modifications of Fehling's solution were next tried. The best results were obtained with a reagent made up with copper acetate, sodium potassium tartrate, and sodium hydroxide. When this was added to a solution containing about 0·25 grm. of gum arabic in 40 cc. of water, there was no precipitation, or at most a slight turbidity. An amount of 95 per cent alcohol equal to the volume of the mixed solutions was then added, with vigorous stirring. This resulted in the formation of a fine-grained precipitate that could be filtered off and washed with comparative ease. It was dried, weighed, ignited, and the ash weighed. The results by this method varied a few per cent below and above 100.

Copper acetate was chosen for making up the reagent because no sodium sulphate or other salt insoluble in alcohol of the strength used could be formed. Even this reagent is not ideal, and the final step taken is described below.

7. *Method Finally Adopted.*—Copper acetate dissolved in ammonia possesses certain advantages over all the other solutions employed. In order to ascertain the best conditions for precipitation, a few preliminary tests were made. One-quarter grm. of gum arabic was dissolved in 50 cc. of water, 25 cc. of ammoniacal copper acetate solution (see below) added, and then enough alcohol to give the required percentage of the total volume of the mix-

ture. Thirty per cent of alcohol gave no precipitate. With 40 per cent there was a faint precipitate, so finely-divided that it was practically impossible to filter. With 50, 60, and 70 per cent of alcohol respectively, dense and easily filtered precipitates were formed. The addition of more alcohol to the filtrates from these three caused no further precipitation. These precipitates gave on ignition the following amounts of ash, practically all cupric oxide :—

Percentage of alcohol employed.	50.	60.	70.
Ash (grm.)	0·0412	0·0436	0·0544
	0·0402	0·0446	0·0564
	0·0398	0·0452	0·0548
Averages	0·0404	0·0445	0·0552

From this it will be seen that in the presence of 50 per cent of alcohol the gum is precipitated quantitatively, and carries down with it less occluded matter than when the mixture contains more alcohol.

The following procedure was finally adopted for the determination of gum arabic:—Fifty grms. of copper acetate were dissolved in water, an excess of ammonia added, and the solution diluted to 1000 cc., using water and alcohol in such proportions that the final solution contained 50 per cent of alcohol. For each determination a 50 cc. portion of a gum arabic solution, representing 0·25 grm. of gum, was pipetted into a 250 cc. beaker, an equal volume of alcohol added, and then 25 cc. of the copper reagent, with constant stirring. The precipitate was allowed to settle, was filtered on a tared paper, washed with 50 per cent alcohol containing ammonia, then with 75 per cent, and finally with 95 per cent alcohol. It was dried to constant weight at 105°, ignited in a porcelain crucible, and the ash weighed. The amount of ash was deducted from the weight of the original precipitate, and the difference called "net gum arabic." The amount of moisture in the gum originally taken for analysis must be allowed for. This is determined by drying in a current of hydrogen at 105°. No allowance is made for the potassium and calcium which form an integral part of the gum. These may be, to some extent, retained in the precipitate, and therefore be included in the ash. Any error that may be introduced by neglecting this is small and very much less than the error inherent in the method.

In some of the preliminary work the gum-copper precipitate was dried at 95° and then at 105°. The additional loss in weight at the higher temperature was usually about 3 or 4 mgrms., or 1·5 per cent. The following results were obtained with 0·25 grm. portions of gum .—

Results obtained by the Ammonia Copper Sulphate Method.

Series.	A.	B.	C.	D.
Percentage of gum found ..	96·6	100·1	100·4	101·6
	98·0	99·0	101·2	102·8
	96·9	98·3	99·1	103·3
	98·4	99·3	99·7	—
	96·7	100·7	98·8	—
Averages	97·3	99·5	99·9	102·6
General average.. ..	99·5			

It is evident from an inspection of the figures that the method as finally modified is capable of giving results as accurate as could be expected. It is realised, however, that much work could yet be done upon mixtures of gum arabic with ghatti, dextrin, &c., as well as upon mucilages of known composition. A few preliminary determinations, made while Fehling's solution was still being experimented with, indicate that dextrin and ghatti tend to be carried down with gum arabic. At the same time a sample of mucilage was prepared according to the formula in the U.S. Pharmacopœia, from this the gum was precipitated with strong alcohol, dried, and analysed. The net gum found in four determinations was about 91 per cent. This low result may be due to a fault of the method or to partial hydrolysis of the gum.

The publication of the results so far obtained has been so long delayed, and the opportunity to complete the work seems so remote, that it has been decided to present this paper without further postponement.

Summary

The most characteristic qualitative test for gum arabic is the precipitate formed with basic lead acetate. Mixtures of copper sulphate and sodium hydroxide, and of neutral ferric chloride and alcohol are of value as confirmatory tests. A summary of the more important methods that have been proposed for the estimation of gum arabic is followed by a description of the steps that led the authors to the use of alcoholic copper acetate-ammonia solution for this determination.

ON THE CONSTITUENTS OF POISON IVY (*RHUS TOXICODENDRON*).

By S. F. ACREE.

The interesting article previously inserted (Chem. News cxiv., 185) was kindly referred to me by the author for the publication of a simultaneous note. As Dr. Syme died several years ago and his note-books are not available, and the busy life makes us forget the details of work finished ten years before, the writer can give only a general statement regarding the preceding note by McNair This article has been referred to him.

Two points in McNair's paper will be discussed—namely, (1) the logic and (2) the facts, imperfections in either of which lead, save by accident, to wrong conclusions. Syme had considerable knowledge of this difficult plant work and was peculiarly adapted to this kind of problem. He worked on the *ether extract* of the *leaves and flowers* of *Rhus toxicodendron*, whereas McNair worked on the *gasoline extract* of the *limbs* of *another species*, *Rhus diversiloba*, and, as *might* be expected, secured *different results*. He therefore concluded that *Syme's* work is wrong. The only other comment to be added is that McNair may not have given sufficient weight to the well-known fact that the botanical differences in species may often be detected only with difficulty whereas the chemical differences may differ widely. This phase of the work has been discussed a number of times, especially in an illuminating article by Schorger ("Chemistry as an Aid in the Identification of Species," *Proc. Soc. Am. Forest.*, 1916, xi., 33), to whom I am indebted for the following *résumé*.

It is well known that the same plant yields very different volatile oils in different localities having different soils, moisture conditions, and climates. The Lavender plant (*Lavandula vera*) of France gives an oil containing 40 to 42 per cent of esters, whereas in England the same species gives an oil whose ester content never exceeds 10 per cent. The fennel oil produced in Saxony, Galicia, and Moravia contains fenchone, which is entirely absent in the Macedonian product. Clover (*Phil. Journ. Sci.*, 1907, 2A, 1) and Bacon (*Ibid.*, 1909, 4A, 93) showed that different trees of the species *Canarium luzonicum*, A. Gray, gave resins which yielded oils consisting either of pure terpinene, limonene, or phellandrene. Bourquelot and Fichtenholz (*Journ. Pharm. Chim.*, 1911, vii., 3, 5) found the glucoside arbutine in the leaves of *Pyrus communis*, but none could be detected in the leaves of *Cydonia vulgaris*, Pers., *Malus communis*, Link., *Sorbus aucauparia*, L., or *S. torminalis*, Crantz, all of which were formerly classed as *Pyrus*.

Another very interesting case is a set of the oils obtained by Schorger from Jeffrey pine, western yellow pine, and the "cross variety" pine, which resemble each other so closely that it is difficult to tell them apart by botanical methods. The oil from the Jeffrey pine boils at about 98° and contains 95 per cent of heptane. The oil from the typical western yellow pine (*P. ponderosa*) boils at 164° and contains no heptane and yields about 65 per cent of β-pinene. The "cross variety" of the western yellow pine boils at 165° and contains β-pinene, and limonene in some cases. The "bastard" pine boils at 156° and contains no heptane but about 65 per cent of α-pinene. The western yellow pine (*P. ponderosa scopulorum*) of Arizona boils at 157° and contains no heptane but about 65 per cent of α-pinene. The optical rotations of these substances vary in a similar way.

Schorger has discovered some other facts of great interest in this connection. The oleoresin from both *P. jeffreyi* and *P. sabiniana* (*Bull.* 119 Forest Service; *Journ. Ind. Eng. Chem.*, 1913, v., 971) give heptane on distillation. The oil distilled from the needles and twigs of *P. sabiniana* was found to contain only 3 per cent of heptane, the remainder consisting of *terpenes* (*Journ. Ind. Eng. Chem.*, 1915, vii., 24). This small amount of heptane may doubtless be that which occurred in the woody portion of the twigs. *Many other cases are known in which the leaves contain compounds not found in the bodywood, bark, or roots of the same tree, and vice versa.*

This observation and the results given above show beyond question that the phytochemical processes occurring in the needles and in the wood of these conifers are entirely different. This being the case it would be dangerous to assume that the poison occurring in the *leaves and flowers* of *Rhus toxicodendron* should be found in the *bodywood* of this plant, and certainly it is entirely inadmissible to assume that this same poison or the same non-toxic constituents should be found in the *limbs* of an entirely different species, *Rhus diversiloba.*

McNair's discussion of the solubilities of complex glucosides and their relation to the solubilities of the components, as well as his reasoning on the relation of the toxicity of a complex organic compound to the toxicity of the constituents, or *vice versa*, will find many opponents among the pharmacologists and plant chemists. Any good book, such as Fraenkel's "Arzneimittelsynthese," gives numberless illustrations to show that the general relationships assumed by McNair cannot hold. Derivatives of saccharin lose the sweet taste. The local anæsthetic cocaine is made up of a combination of ecgonine, benzoic acid, and methyl alcohol, no one of which has the same action as the cocaine. The examples could be multiplied indefinitely, as I am assured by my friends Loevenhart and Kremers.

Coming to the discussion of (2), Syme's *facts*, we note again that because McNair *failed* to find gallic acid, fisetin, and rhamnose as free or combined constituents of the *gasoline extract* of the *limbs* of *Rhus diversiloba* he concludes that Syme could not have found them in the *ether extract* of the *leaves and flowers* of *another species Rhus toxicodendron.*

McNair criticises Syme's work on the hydrolysis products of the poisonous tar or wax after simply making a few negative colour tests. After noting that McNair himself did not isolate anything more crystalline than a "dark liquid mystery," which still remains so, let us review what Syme actually obtained in the crystalline state. From the aqueous extract of the *total* poisonous tar Syme obtained crystalline potassium, barium, and sodium salts, and crystalline gallic acid, melting-point 230°, and converted it into the crystalline ethyl ester which melted at 156—9°, whether alone or mixed with the ethyl ester prepared from Kahlbaum's gallic acid. He then subjected the gallic acid to the characteristic colour and other tests discussed in his dissertation. The most concentrated "poisonous tar, gum, or wax" was called the "poison" for brevity, but was obviously never considered to be "crystalline" and pure. This substance on hydrolysis gave the same characteristic colour and other tests for gallic acid, but the amount of "poison" available was too small to attempt to isolate crystals, and it was used chiefly for the more valuable toxicity and other tests.

Turning to the dye-stuff, fisetin, which McNair could not find in another species, we note that Dr. Syme did isolate crystalline fisetin from the total tar, studied its colour reactions, and even decomposed 2 grms. of it into phloroglucinol and protocatechuic acid. Syme was already familiar with fisetin, and I believe had samples for comparison. As stated above, the amount of the most concentrated "poison" was too small to allow Syme to isolate crystalline fisetin from its hydrolysis products, but he obtained the same characteristic colour and other tests found for his crystalline fisetin.

Coming to rhamnose we found that Syme discussed fully the difficulties of obtaining this sugar, as indeed most sugars, in the crystalline state. He had to be content, therefore, with characteristic colour and other tests worked out for crystalline rhamnose, including of course the conversion into methyl furfural (Dissertation, p. 23). Of course a number of the methyl pentoses discovered since that time give a number of similar tests.

As stated above, the "poison" was a tar, wax, or gum, and Warren believes that this "poison" may have been a complex mixture containing the pure poison or poisons and one or more non-toxic glucosides which can yield the gallic acid, fisetin, and rhamnose. Warren and McNair then agree with Syme's Paragraph 3, p. 563, *Journ. Biol. Chem.*, ii. "In this experiment gallic acid and fisetin, and probably sugar, were formed by decomposition of the poisonous gum with acetic acid, the acid found in the plant by Pfaff. The presence of free gallic acid, fisetin, and rhamnose in the plant can be explained by the natural *hydrolysis of a complex gum or tar or a constituent thereof* (italics new). The poisonous property is lost in the general rearrangement which takes place during hydrolysis." This conclusion was so obvious that it never occurred to Syme or the writer that any other conclusion could be drawn from the work. Any organic chemist knows that such a tar is a mixture, and Syme never for a moment desired to word his articles in such a way that the reader would be left under the impression that a "pure poison" could be obtained in this way. The whole object of this work was to isolate the poison in some fraction or fractions, and study these fractions with the view (1) of measuring the toxicity and finding a method ($KMnO_4$) for curing the wounds, and with the aims (2) of isolating and synthesising the real poison or poisons. The work was discontinued because the very small amount of "poison" in the 100 dols. worth of "total poison or tar" available made the further prosecution of the problem appear too expensive. We should indeed be glad to see anyone with the necessary funds continue this research and synthesise the pure poison or poisons. Success in this direction would mean much toward the solution of a problem which causes a great deal of human suffering.

Summary.

1. McNair's reasoning that the limbs of *Rhus diversiloba* should contain the same toxic and non-toxic constituents found in the leaves and flowers of another species, *Rhus toxicodendron*, in another locality and climate is against all the well-known evidence, because:—

(*a*) The botanical differences in species may often be detected only with difficulty while the chemical constituents may vary widely.

(*b*) The same species gives different substances in different localities and climates.

(*c*) The constituents found in the leaves of a given species are generally *not* identical with those found in the *limbs of the same plant*, much less of a different species under different conditions.

2. It is highly probable that Syme's "purified poisonous tar, gum, or wax" was a mixture of toxic and non-toxic materials. Symes "purified" the material as far as possible, and when it gave out suspended the work on account of the expense. Although his description of the "purified poisonous tar, gum, or wax" and its reactions was in some places perhaps confusing, Syme did not believe that his "purified poison" was not a mixture. It is highly desirable to have the studies on all these toxic plants continued.—*Journal of the American Chemical Society*, xxxviii., No. 7.

THE RELATIVE DENSITIES OF ALKALI-METAL AMALGAMS AND MERCURY.

By JAMES R. WITHROW.

Attention is called to erroneous impressions, concerning the relative densities of alkali-metal amalgams and mercury, which are encouraged by descriptions of the preparation of such amalgams in the literature and standard handbooks.

Arlt ("A Process and Apparatus for effecting Electrolysis —Liquid Electrodes"), F. W. Goldby (from O. Arlt, Goerlitz, Germany, Eng. Pat. 15,129, July 8, 1896; *Journ. Soc. Chem. Ind.*, 1896, xvi., 908; *Zeit. Electrochem.*, 1897, iii., 300), Nernst (*Zeit. Electrochem.*, 1897, iii., 309), and Kerp (*Zeit. Anorg. Chem.*, 1898, xvii., 300), each used a falling stream of mercury as cathode in producing alkali amalgams. Kerp was aiming at the production of a solid alkali amalgam by ultimately separating the spongy mass, a mixture of solid and liquid amalgam, which he obtained in the receiver of the apparatus, by means of a Gooch crucible. He gives an illustration of his apparatus (*loc. cit.*). A noticeable feature of this illustration is that the solid potassium amalgam is pictured and *labelled*, as settling or collecting in the bottom of the receiver *beneath* the layer of mercury and dilute amalgam. Later, E. S. Shepherd (*Journ. Phys. Chem.*, 1903, vii., 29) described his lecture table experiment for the production of solid sodium amalgam in which he uses a special device to overcome the fact, pointed out by him, that sodium amalgam is *lighter* than mercury and floats on the top. Shepherd cited the work of Kerp, but did not call attention to the anomalous behaviour imputed to potassium amalgam by the latter. Although Shepherd's work should raise serious question concerning the relative densities of all alkali-metal amalgams and mercury, the "Handbuch der Anorganischen Chemie," by Abegg (vol. ii., II., 579), copies the picture given by Kerp just as he gave it in his original article, indicating that the solid amalgam settles to the bottom with a layer of dilute amalgam remaining above it.

There appear to be no actual values in the literature for the density of these various amalgams. The work of Maey (*Zeit. Phys. Chem.*, 1899, xxix., 127), tables from which appear in Abegg itself (vol. ii., II., 582), gives specific volumes for alkali amalgams of different concentrations, which are the only series of values in the neighbourhood of the range of composition in Kerp's work. From these values densities may be calculated, and it is seen that the heaviest potassium amalgam given (0·184 per cent K) has a density of 13·3707, the heaviest sodium amalgam (0·103 per cent Na) a density of 13·448, and lithium amalgam (0·0301 per cent Li), of 13·5116 when mercury has a density of 13·5956. These values calculated from the work of Maey show the amalgams to be distinctly lighter than metallic mercury. These calculated values are for highly dilute amalgams which are probably solutions of solid amalgams in mercury, so that an actual solid amalgam might be heavier than these specifically light dilute amalgams. That this is *probably* not true at any point appears from an inspection of Maey's complete table of specific volumes, which runs up to high alkali concentrations. The values become progresively greater, showing that the densities corresponding must get progressively lighter. No overlapping or displacement of the curve takes place as would be the case if any solid amalgam separating should contract sufficiently to make it specifically heavier than the mother-liquor or more dilute amalgam. Vanstone (Chemical News, 1911, ciii., 207) condemns Maey's results as not accurate, but like Shepherd, he worked with sodium only, and gives but one observation in the neighbourhood of Kerp's operation zone. The results over Vanstone's whole range, however, agree so closely with Maey's that they do not alter the above deductions from Maey's results. For instance, a recalculation of Vanstone's data for his heaviest amalgam (2·26 per cent Na) which was a solid amalgam, gives a density of 11·733 at 17° C., which is much lighter than mercury, and confirms Shepherd.

These apparent contradictions of the illustrations in the work of Kerp and Abegg do not insure that even some outside factor was not reversing the probable natural properties of these amalgams in Kerp's case. Elevation of temperature might possibly reverse the relative densities of mercury and some of these amalgams. There is perhaps no reason why there should not exist some alkali amalgams heavier than mercury, but in the writer's experience with these amalgams he has never noticed such cases. Isolated crystals of amalgam, for instance, might grow attached to the walls or bottom of the vessel and beneath the mercury, in spite of their lighter density. A spongy mass of mixed solid and liquid amalgam might appear to rest on the bottom.

When, in investigating these possibilities, one placed the mercury and amalgam mixture in a suitable vessel and forced his hand or a scoop below the surface, he could feel the pasty amalgam at or just under the surface, and could lift some of it out. Solid alkali amalgam, both potassium and sodium, made by the method of both Kerp and Shepherd, in pieces an inch or more in diameter, were placed in mercury. These firm pieces floated in the mercury like ice in water, and are distinctly visible, projecting just above the surface, and can be felt with a rod or the finger, for the mercury is not transparent as is the liquid in the ice and water case. When the solid amalgam is in isolated crystals or paste form it does not project above the surface of the mercury. No grounds of any kind were, however, found for assuming that solid amalgam ever stayed on the bottom beneath a layer of mercury or dilute amalgams. The ease, however, with which amalgam adheres to glass could readily deceive one into thinking when he poured out a mixture of solid and liquid amalgam, that the solid amalgam adhering to the sides and bottom of the vessel had always been there and therefore was heavier than mercury.

The fact that sodium amalgam is distinctly lighter than metallic mercury has long been the conscious basis of experimental effort among industrial chemists who have worked in the field of mercury cathode cells. This rising of sodium amalgam to the top, in a mixture with mercury, causes certain engineering difficulties in the otherwise simple manipulation of the Castner-Kellner processes for making sodium hydroxide. Great trouble is encountered in endeavouring to circumvent the difficulties caused by this very fact. Complicated industrial chemical machines have been devised to overcome this factor, such, for instance, as the Whiting cell (*Trans. Am. Electrochem. Soc.*, 1912, xvii., 327), which operates on the separatory funnel principle, or the Wildermann cell and others.

The recalculated data of Maey's are so well supported by the experiments presented here, as to indicate strongly that potassium amalgam is not anomalous in its effective density, but, like sodium amalgam, is lighter than mercury. It seems, therefore, that when a book of the value of Abegg assists in giving the impression that solid amalgam settles to the bottom, attention should be called to the matter.—*Journal of Physical Chemistry*, xx., No. 6.

NOTICES OF BOOKS.

A Method for the Identification of Pure Organic Compounds. Volume II. By Samuel Parsons Mulliken, Ph.D. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. ix. + 327. Price 21s. net.

The second volume of this valuable work treats of the systematic analysis of compounds of carbon, nitrogen, hydrogen, and oxygen. About four thousand such compounds are enumerated, and the author had a formidable task to perform in working out schemes which would lead to the identification of each one with the minimum expenditure of time and trouble and the maximum certainty regarding the result. The plan adopted was identical with that described in the first volume. The unknown substance has first to be placed in its proper group among (i.) acidic, (ii.) basic, (iii.) neutral colourless compounds, or (iv.) coloured compounds. The substances are then tabulated in order of ascending melting-point or boiling-point, and the identification of each by characteristic tests is fully described. An example of the identification of a typical and somewhat complicated substance makes it perfectly clear how the book is to be used, and although the process of ascertaining the nature of an unknown might be lengthy by the author's scheme there would appear to be practically no possibility of error or of uncertainty in the result. The classes of compounds dealt with in this volume include the alkaloids, many highly important drugs, explosives, and substances employed in dyeing, and the book will be found a very valuable addition to the library of the analytical chemist. The author is to be congratulated upon having carried through a very important piece of work, which included not only the devising of new tests but also the correction of many errors in descriptions of constants and of other properties.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xix.-xx., No. 8, 1916.

Contribution to the Knowledge of Perkin's Reaction. New Method of Preparing Substituted Cinnamic Acids.—S. Reich and P. Chaskelis.—Perkin and Nef have supposed that in Perkin's reaction benzylidene diacetate is formed as an intermediate product. One of the authors has confirmed this view by obtaining the diacetate of 2.6 dichlorobenzylidene in the preparation of 2.6-dichloro-cinnamic acid. It has been shown that the diacetate does not owe its formation to a reaction accompanying that which gives rise to the acid, but that it must be regarded as an intermediate product in the formation of the acid. Fittig, however, has shown that in certain cases Perkin's reaction can take place in the absence of an anhydride, as, for example, when benzoic aldehyde is heated with sodium malonate in presence of acetic acid. Hence it must be admitted that the reaction can be effected by two different processes. Sodium malonate which contains very mobile hydrogen is capable of reacting with an aldehyde even without the aid of acetic anhydride, which is necessary in the case of a salt the hydrogen of which is not mobile. This view of Perkin's reaction has led the authors to the discovery of a new method of preparing cinnamic acids substituted in the benzene nucleus. Thiele has shown that toluene and its substitution derivatives can be oxidised by chromic anhydride in sulphuric solution in presence of acetic anhydride. The diacetates of the aldehydes are thus obtained, and on saponification give the aldehydes. When the cinnamic acids are to be prepared it is unnecessary to transform the diacetates into aldehydes. The raw product of oxidation, which consists of a mixture of diacetate and unchanged hydrocarbon, is heated with acetic anhydride and sodium acetate. The diacetate is then totally transformed into cinnamic acid, and the hydrocarbon is separated from the acid by distillation in a current of steam.

New Heterogeneous Chain containing Arsenic in the Nucleus: Methylarsepedine.—Enrique V. Zappi.—The author suggests the names arsedine and arsepidine for the arsenic derivatives of pyridine and piperidine. Thus cyclopentamethylene methyl arsine would be called methylarsepedine. This substance the author has prepared by adding dichloromethylarsine to an ethereal suspension of the magnesium derivative of 1.5 dichloropentane. A vigorous reaction occurs, and a white precipitate is formed, which is decomposed by water setting free methylarsepedine. When the ethereal solution is distilled methylarsepedine is obtained and a liquid residue consisting of condensation products of methyl-arsepedine.

MISCELLANEOUS.

Empire Industrial Policy.—The Prime Minister of New Zealand, the Right Hon. W. F. Massey, has promised to speak at a luncheon of the British Empire Producers' Organisation at the Waldorf Hotel on Tuesday next, when Sir Henry Birchenough, K.C.M.G., will preside. The guests will also be addressed by Mr. F. R. Davenport, Chairman of the British Electrical and Allied Manufacturers' Association, which represents various important sections of the engineering industry. Delegates of Canadian, Australian, South African, Indian, West Indian, and other Dominion industrial interests will be present, and the list of great industries represented will include railway and shipping, sugar, jute, tea, timber, and rubber, general agriculture, engineering, chemicals, textile, shipbuilding, leather, and other manufactures, besides technical institutions and chambers of commerce. It is the aim of the British Empire Producers' Organisation to co-ordinate the efforts of sectional trade associationr and further the gradual formation of a practical Imperial economic system under which British national resources and manufactures will be developed for the benefit of the whole population.

MEETINGS FOR THE WEEK.

Wednesday, Nov. 1st.—Society of Public Analysts, 8. "Quantitative Microscopy," by T. E. Wallis. "Formula for Converting Zeiss Butyro-Refractometer Readings into Refractive Indices," by C. C. Roberts. "Criticism of Vaubel's Bromine Values," by C. Revis and H. R Burnett.

Thursday, 2nd.—Royal Society. "Waves in an Elastic Plate," by H. Lamb. "Multiple Integrals" and "The Order of Magnitude of the Coefficients of a Fourier Series," by W. H. Young. "Determination of the Heat of Vaporisation of Water at 100° C. and 1 Atmosphere Pressure in terms of the Mean Calorie," by T. C. Sutton. "Mechanical Relations of the Energy of Magnetisation," by G. H. Livens.

— — Chemical Society, 8. "Overvoltage Tables—Part IV., The Theories of Overvoltage and Passivity," by E. Newbery. "Studies of the Carbonates—Part II., Hydrolysis of Sodium Carbonate and Bicarconate, and the Ionisation Constants of Carbonic Acid," by C. A. Seyler and P. V. Lloyd. "Synthesis of Hydroxyquercetin," by M. Nierenstein. "Reaction between Methyl Iodide and some Metallic Cyanides" and "Some Reactions produced by Mercuric Iodide," by E. G. J. Hartley. "The Dual Theory of Acid Catalysis—a comparison of the Activities of certain Strong Acids," by H. M. Dawson and T. W. Crann.

THE CHEMICAL NEWS.

VOL. CXIV., No. 2971.

SENSITIVENESS TO DETONATION OF TRINITROTOLUENE AND TETRANITROMETHYLANILIN.[*]

By GUY B. TAYLOR and WILLARD C. COPE.

(Concluded from p. 204).

Comments on Results.

IN every case of incomplete detonation, as indicated by a small crushing effect, a part of the charge unexploded was found in the sand. The criterion of the minimum charge was five complete detonations with no failures. The minimum charges of fulminate-chlorate (90 : 10) primer that caused complete detonation of the different mixtures of explosive, as shown by Table A, were as follows:—

Minimum Charges of Fulminate-chlorate (90 : 10) *Primer that caused complete Detonation of different Mixtures of Explosive.*

Explosive. T.N.T. Per cent.	Explosive. Tetryl. Per cent.	Smallest weight of primer that caused complete detonation of explosive. Grm.
100	0	0·25
90	10	0·22
80	20	0·21
50	50	0·20
0	100	0·19

Besides the mixtures made by fusing the T.N.T. and the tetryl a mixture containing 20 per cent tetryl and 80 per cent T.N.T. was made by mechanically mixing the finely ground constituents. The minimum charge of primer that caused complete detonation of this mixture was 0·21 grm., or the same as that for the fused mixture. It would seem unnecessary to assume the existence of a compound between the two substances to account for the increase of sensitiveness of their mixtures. The results with a priming charge of 0·32 grm. indicated a slight increase of strength with increasing tetryl content.

The sensitiveness of T.N.T.-tetryl mixtures to moist fulminate mixture was also determined. A number of detonators were made up as above described containing charges of 0·4 grm. base charge and 0·32 grm. of 90 : 10 priming charge. These were stored over water and tested from time to time. The pure T.N.T. failed when the detonator had taken up 0·0030 grm. of moisture; 10 per cent tetryl detonated when the moisture content was 0·0037 grm. and failed when the moisture content was 0·0048 grm.; 50 per cent tetryl detonated when the moisture content was 0·0048 grm. and failed when the moisture content was 0·0055; and the pure tetryl cap still detonated with a moisture absorption of 0·0062 grm.

Lead hydronitride, or lead azide (PbN_6), seems to have a distinct preference for detonating tetryl. The authors have found that as little as 1 mgrm. will often detonate tetryl and that 0·1 grm. will always do so. The minimum charge for T.N.T. under a loading pressure of 200 atmospheres is 0·23 grm.; with a pressure of 400 atmospheres it is about 0·15 grm. Martin found the minimum charge to be 0·09 grm. under a loading pressure of about 1000 atmopheres.

Conclusions.

T.N.T. (trinitrotoluene) is much less sensitive to detonation than tetryl (trinitromethylnitramine or tetranitromethylanilin). The sensitiveness of the former is increased by admixture of the latter. These two compounds, varying widely in sensitiveness, are suitable substances on which to test the efficiency of initial priming compositions. In Bureau of Mines reports that are to follow the relative efficiencies of various mixtures of mercury fulminate and other substances in detonating these two compounds will be given.

Note.

On account of the present high price of mercury used in the manufacture of mercury fulminate detonators have greatly advanced in price. Manufacturers are seeking a substitute to partly replace the fulminate. By use of a suitable base charge and of a fulminate-chlorate mixture as a primer in the reinforced detonator about one-half as much fulminate is required for a cap of given strength. Commercial blasting caps have been manufactured containing both T.N.T. and tetryl as the base charge. About 0·40 grm. of base charge and 0·32 grm. of 90 : 10 fulminate-chlorate primer make a cap of the No. 6 grade. It is important to use as a factor of safety about 50 per cent excess primer above the minimum quantity required for complete detonation of the base charge. It is also important to use a base charge not too insensitive to slightly moist fulminate. Any explosive proposed for use as a base charge should be thoroughly tested to meet any possible conditions of treatment or storage to which the blasting caps are likely to be exposed in practical work, for the failure of a single cap may be a serious matter. On account of its insensitiveness to slightly moist fulminate T.N.T. has proven an unsatisfactory base charge.

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[*] *Technical Paper 145, Bureau of Mines, U.S.A.*

Publications on Explosives for Mining and Accidents therefrom.

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Bulletin 59. "Investigations of Detonators and Electric Detonators." By Clarence Hall and S. P. Howell. 1913. 73 pp., 7 pls., 5 figs.

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Titration of Solution of Oxalic Acid.—M. Blanchetière.—The author has investigated different methods of analysing solutions of oxalic acid and finds that the best method is precipitation as calcium oxalate, followed by weighing as carbonate after recarbonisation. Alkalimetric titration of the warm solution, or iodometric titration in presence of sulphuric acid, can very satisfactorily be employed, being accurate and very quick. A fairly accurate method is the direct weighing of oxalic acid in a liquid or standardisation by alkalimetry in the cold. The iodometric method in presence of a standard picric solution is not satisfactory.—*Bull. Soc. Chim.*, xix.-xx., 8.

CARBONIC ACID FROM NATIVE LIMESTONES.*

By Prof. A. P. LIDOFF.

1. The weight of the gas of the natural limestones is not always that of the carbonic acid, and often, as, for instance, in the calcspar, it is much less; upon an average, taken from thirteen examinations, the weight of a litre of it (by 0/760) is equal to 1·9125 grms.

2. The weight of the gas of another crystalline kind of the aragonite is almost just the same as that of the carbonic acid.

3. Likewise the weight of the gas of the friable limestones, chalk, tufaceous, and mussel limestones, &c., is almost completely equal to that of the carbonic acid.

4. The weight of the gas obtained from the marbles and very dense and old limestones is, upon an average, greater than that of the calcspar, but much less than that of the friable ones and argonite, and is upon average equal to 1·933.

5. This mentioned inconstancy of the weight of the gas obtained from different limestones suggest us an idea, that many limestones beside the carbonic acid contain also a more or less considerable quantity of α-oxan, OCN.

ESTIMATION OF PHENACETIN AND SALOL IN ADMIXTURE.

By W. O. EMERY, G. C. SPENCER, and C. C. LEFEBVRE.

Introduction.

In the course of certain analytical work on medicinial tablets, we were considerably handicapped for a time through lack of a quantitative method for estimating phenacetin and salol in admixture. Accordingly, efforts were directed first to their separation, and second to their individual determination. It was found that a satisfactory separation could be effected by treatment either with dilute sulphuric acid, or with sodium hydroxide of definite concentration, followed by extraction with chloroform.

The separation proper, therefore, follows two distinct lines of procedure, involving, on the one hand, the acid hydrolysis of phenacetin, on the other the alkaline hydrolysis of salol. In the first instance, the direct estimation of phenacetin only is contemplated, the salol being determined by difference in all cases where the combined weight of both constituents is known or can be conveniently ascertained. In this procedure, the phenacetin is temporarily converted into phenetidine sulphate and acetic acid, while in the case of salol partial volatilisation results during the process of digestion. The phenetidine salt, by virtue of its insolubility in chloroform, is readily freed from further contaminating salol by treatment with that solvent, then by means of acetic anhydride and sodium bicarbonate reconverted into phenacetin, the latter being subsequently isolated and weighed.

In the case of alkaline hydrolysis, the salol is first converted into sodium salicylate and phenolate, from which the phenacetin is easily separated and subsequently recovered by extraction with chloroform. The salol is thereupon treated in rotation with standard bromine solution in excess, hydrochloric acid, potassium iodide, and sodium thiosulphate. The principal reactions involved in the process and which serve as the basis for the calculation of results are:—

$$HOC_6H_4CO.OC_6H_5 + 3NaOH = \\ = NaOC_6H_4CO_2Na + C_6H_5ONa + 2H_2O,$$

$$C_6H_5OH + 4Br_2 = C_6H_2Br_3OBr + 4HBr,$$

$$HOC_6H_4CO.OH + 4Br_2 = C_6H_2Br_3OBr + 4HBr + CO_2,$$

$$C_6H_2Br_3OBr + 2HI = C_6H_2Br_3OH + HBr + I_2,$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6,$$

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* Summary of an elaborate paper printed in Russian.

from which it follows that 12 atoms of bromine are expended on every atom of salol, and that titration of the iodine liberated by the unexpended bromine affords sufficient data for the estimation of salol.

First Method—Acid Hydrolysis.

Phenacetin.—If the sample is in pill or tablet form, ascertain the weight of 20 or more, reduce to a fine powder, and transfer to a small tube or specimen bottle which can be kept tightly closed with a cork or glass stopper. Weigh out on a small (5·5 cm.) tared filter an amount of the sample equal to, or a convenient multiple of, the average weight of such pill or tablet, wash with successive small portions of chloroform, in quantity about 40 cc., sufficient at least to insure the complete extraction of all the phenacetin and salol present in the mixture. Collect the solvent in a tared 100 cc. beaker, evaporating by means of a blast to apparent dryness. During this operation, the beaker may, with advantage, be allowed to stand on a warm plate (50—60°) without danger of undue loss of solid substance. Permit the beaker to remain twenty-four hours in the open at the ordinary temperature, weigh several times until practically constant, then transfer the crystalline residue, by dissolving in and washing with sufficient chloroform to a 50 cc. lipped Erlenmeyer, evaporate solvent by means of a blast and gentle heat, add 10 cc. dilute sulphuric acid (1 : 10), and digest at full steam-bath heat until the liquid is reduced one-half. Add 10 cc. of water, continue the digestion as before, add a second 10 cc. of water, and evaporate to 5 cc. Transfer the residual liquid by pouring and washing with about 20 cc. of water to a small separatory funnel of the Squibb type, and extract in rotation with 15, 10, and 5 cc. chloroform, washing each portion as obtained with 5 cc. water in a second separator, in order to recover traces of phenetidine sulphate possibly taken up by the chloroform, finally rejecting the latter, since it contains all the salol not previously eliminated during the process of digestion.

To the aqueous acid solution of phenetidine sulphate in the first separatory funnel, into which also the wash water from the second separator has been drawn, add sodium bicarbonate in small portions until an excess of this reagent persists at the bottom of separator after complete neutralisation of the sulphuric acid. Now add 25 cc. chloroform, and for every 100 mgrms. acetphenetidine or phenacetin known or believed to be present 5 drops of acetic anhydride, shake for some time vigorously, then pass the nearly clarified solvent into a second separator containing 5 cc. water, shake and receive the chloroform in a 200 cc. Erlenmeyer, first passing it through a small (5·5 cm.) dry filter. Distil at gentle heat about 20 cc., returning the latter to the first separator. Augment with 5 cc. fresh chloroform, and repeat the extraction, washing, and filtering as before, then collecting the solvent in the Erlenmeyer, and again distilling until 25 cc. chloroform are obtained. With this portion make a third and final extraction, repeating the operations of washing, filtering, and distilling to the point where about 5 cc. chloroform remain in the Erlenmeyer. Transfer this chloroformic residue by pouring and washing with sufficient fresh chloroform to a tared 50 cc. beaker or crystallising dish, evaporate on a steam or vapour bath to apparent dryness, finally removing any pronounced excess of acetic anhydride by repeated addition of 1 cc. portions of fresh chloroform (to which a drop of alcohol has been added), and subsequent evaporation. Allow the nearly colourless crystalline residue of acetphenetidine or phenacetin to stand some time in the open, or better in a vacuum desiccator over lime, in order to eliminate the last traces of acetic anhydride. Weigh at intervals until constant.

Salol.—To ascertain the quantity of salol present in the sample, subtract the weight of phenacetin as found above from the combined weight of the two ingredients determined in the preliminary separation.

Second Method.—Alkaline Hydrolysis.

Phenacetin.—On a small tared filter weigh out an amount of the sample containing not more than 100 mgrms. salol, exhaust with chloroform as in acid hydrolysis, collecting the solvent in a small lipped Erlenmeyer, Evaporate the chloroform by means of a blast and without applying heat. Add 10 cc. 2·5 per cent sodium hydroxide solution, and heat five minutes on a steam or vapour bath at the temperature of boiling water. At the end of this period remove from bath, and cool quickly to room temperature in running water in order to reduce to a minimum any tendency of the phenacetin to undergo partial hydrolysis. Transfer the liquid to a separatory funnel by pouring and washing with a minimum of water, finally rinsing out the flask with the first 20 cc. portion of chloroform used in extraction. Extract the aqueous alkaline solution with three 20 cc. portions of chloroform, washing each portion as obtained consecutively in a second separator with 5 cc. water, prior to passing the solvent through a small dry filter into a 200 cc. Erlenmeyer, from which the combined chloroformic portions are distilled down to a residue of about 5 cc. Transfer the latter by pouring and washing with sufficient fresh chloroform to a small tared beaker or crystallising dish, evaporate the solvent on the steam-bath by the aid of a blast, cool, and weigh the phenacetin at intervals until constant.

Salol.—Transfer both aqueous alkaline solutions from the separatory funnels to a suitable (500 cc.) glass-stoppered bottle, dilute with water to about 200 cc., run in from a a burette an excess (about 45 cc.) of N/7 potassium bromide bromate, followed with 10 cc. concentrated hydrochloric acid, close flask, and shake one minute, then at intervals over a period of one-half hour. At the end of this time add 10 cc. 15 per cent potassium iodide solution, agitating the closed flask at intervals for fifteen minutes. Titrate the free iodine with standard thiosulphate (preferably N/7), previously adjusted to the standard bromine solution, 1 cc. of which is equivalent to 0·002548 grm. salol. From the number of cc. standard bromine solution expended, calculate the salol on the basis of 12 atoms of bromine to 1 molecule of salol.

SERIES 1.—*Acid Hydrolysis.*

Phenacetin. Grm.	Salol. Grm.	Phenacetin recovery. Grm.	Per cent.	Salol recovery. Grm.	Per cent.
0·1028	0·1159	0·1028	100·00	0·1159	100·00
0·1021	0·0996	0·1021	100·00	0·0996	100·00
0·1006	0·1048	0·1009	100·39	0·1045	99·71
0·1015	0·1015	0·1010	99·50	0·1020	100·49
0·1010	0·1044	0·1008	99·80	0·1046	100·19
0·1042	0·1004	0·1043	100·09	0·1003	99·92
0·1015	0·1001	0·1016	100·09	0·1000	99·90
0·1069	0·1186	0·1071	100·18	0·1184	99·83
0·1010	0·1174	0·1009	99·89	0·1175	100·09
0·0996	0·1014	0·0998	100·20	0·1012	99·79
0·1103	0·1036	0·1101	99·82	0·1038	100·19
0·2000	0·2000	0·1999	99·95	0·2001	100·05
0·1000	0·2000	0·0995	99·50	0·2005	100·25
0·2000	0·1000	0·2004	100·20	0·0996	99·60

SERIES 5.

Sample (*a*). Grm.	Phennacetin + Salol recovery. Grm.	Phenacetin recovery. Grm.	Grains.	Salol recovery. Grm.	Grains.
0·4316	0·3256	0·1621	2·50	0·1635	2·52
0·4316	0·3253	0·1622	2·50	0·1631	2·52
0·4316	0·3257	0·1616	2·49	0·1641	2·53
0·4316	0·3273	0·1626	2·51	0·1647	2·54
0·4316	0·3276	0·1607	2·48	0·1669	2·58
0·4316	0·3268	0·1611	2·49	0·1657	2·56
0·4316	0·3268	0·1637	2·53	0·1631	2·52

SERIES 2.—*Alkaline Hydrolysis.*

Phenacetin. Grm.	Salol. Grm.	Phenacetin recovery.		N/7 Koppeschaar solution cc. expended.	Salol recovery.	
		Grm.	Per cent.		Grm.	Per cent.
—	0·0892	—	—	33·99	0·0882	98·88
—	0·0895	—	—	35·06	0·0891	99·64
—	0·0900	—	—	35·17	0·0894	99·37
—	0·0903	—	—	35·20	0·0893	99·12
0·0125	0·0914	0·0123	98·40	35·27	0·0897	98·13
0·0141	0·0915	0·0142	100·70	35·54	0·0904	98·77
0·0516	0·0513	0·0516	100·00	20·39	0·0518	101·10
0·0516	0·0512	0·0511	99·04	20·59	0·0523	102·30
0·0503	0·0499	0·0509	101·20	19·92	0·0506	101·50
0·0504	0·0508	0·0513	101·70	20·35	0·0517	101·77
0·0495	0·0499	0·0486	98·18	19·69	0·0501	100·40
0·0522	0·0516	0·0503	97·32	20·52	0·0521	100·97
0·0891	0·0884	0·0867	97·30	34·92	0·0890	100·67
0·1020	0·1020	0·1002	98·22	39·37	0·0100	98·33
0·1000	0·1003	0·0983	98·30	38·82	0·9893	98·63
—	0·0880	—	—	34·67	0·0883	100·30
—	0·0896	—	—	35·23	0·0898	100·20
0·0897	0·0892	0·0880	98·11	35·47	0·0904	101·30
—	0·1020	—	—	39·35	0·1002	98·32
0·0977	0·0999	0·0974	99·70	38·63	0·0984	98·55
0·1005	0·1008	0·0999	99·42	39·71	0·1012	100·39
0·0989	0·1012	0·0982	99·28	40·11	0·1022	101·00
0·1011	0·1009	0·1000	98·91	40·00	0·1019	101·00

SERIES 3.

0·1006	0·1000	0·1002	99·60	39·48	0·1006	100·60
0·1039	0·1017	0·1011	97·31	40·00	0·1019	100·20
0·1015	0·1014	0·0987	97·25	39·69	0·1011	99·75
0·0995	0·1200	0·0981	98·60	47·11	0·1200	100·00
0·1012	0·1010	0·0995	98·33	39·64	0·1010	100·00
0·0982	0·0991	0·0966	98·37	38·76	0·0987	99·58
0·1023	0·1000	0·0998	97·57	39·12	0·0997	99·70
0·0996	0·1016	0·0972	97·59	39·86	0·1016	100·00
0·1037	0·0988	0·1013	97·68	38·78	0·0988	100·00

SERIES 4.

0·1032	0·1014	0·1035	100·20	39·60	0·1009	99·54
0·1043	0·0978	0·1045	100·20	38·22	0·0974	99·58
0·1003	0·1011	0·0990	98·70	39·83	0·1015	100·40
0·0911	0·1012	0·0894	98·13	39·93	0·1017	100·49
0·0723	0·1015	0·0710	98·20	40·08	0·1021	100·59
0·0569	0·1020	0·0569	100·00	39·87	0·1016	99·61
0·0799	0·1002	0·0787	98·49	39·47	0·1006	100·30
0·0553	0·1092	0·0550	99·45	42·71	0·1088	99·68

SERIES 6.

Sample (*a*). Grm.	Phenacetin recovery.		N/7 Koppeschaar solution cc. expended.	Salol recovery.	
	Grm.	Grains		Grm.	Grains
0·2700	0·1005	2·48	40·06	0·1022	2·52
0·2700	0·1002	2·47	40·15	0·1023	2·52
0·2700	0·1003	2·47	40·04	0·1021	2·52
0·2641	0·0982	2·48	39·08	0·0996	2·51
0·2641	0·0985	2·48	38·82	0·0989	2·49

(*a*) Average weight of single tablet 0·4316 grm.

Comments and Suggestions.

Tared filters for use in this and similar work may be conveniently prepared as follows:—Fold, adjust in a small short-stemmed funnel, moisten, and press carefully so that the entire rim of filter fits snugly to the glass. After drying, keep in balance case or other suitable dust-proof container, and when needed weigh on a small metal support or glass tripod. It is self-evident that all weighings with tared filters should be made as nearly as possible under comparable conditions. If, for example, the first weight is taken under a hygrometric reading of 50 per cent, the second weighing should be made under approximately similar conditions. This is indispensable when it is desired to estimate the quantity of chloroform insoluble residue in phenacetin-salol tablets or other preparations likely to contain sodium bicarbonate, sugar, starch, talc, or other more or less inert excipients. Experience has shown, however, that a variation in humidity up to 5 per cent at the time of the two weighings would not be productive of material error.

Before carrying out extractions in separatory funnels or introducing liquids therein, the valves should first be "locked" with a drop of water, otherwise losses from capillarity may result.

All distillations of chloroform should be carried out over a wire gauze or asbestos provided with a small opening and heated by a very small flame, the flask being connected with the condenser by means of a small spray trap, if available, similar to the type used in Kjeldahl work.

Phenacetin, being only moderately soluble in hot aqueous media, is accordingly somewhat difficult of hydrolysis. In order therefore to insure its complete conversion to phenetidine sulphate, special attention should be directed to the end that any visible particles of crystalline substance on the sides of flask during the early part of digestion should be gradually brought into solution by gently rotating the flask, and, if necessary, by the occasional addition of a few drops of chloroform.

In order to facilitate the work and minimise errors due to recharging burettes, N/7 solutions are advocated in order that the volume of the thiosulphate required may not exceed the capacity of a 50 cc. burette. The thiosulphate solution is standardised against pure iodine. The strength of the bromine solution may also be determined by the aid of pure acetanilide (*Bull.* 132, Bureau of Chemistry, U.S. Dept. Agr.; *Proc. A.O.A.C.*, p. 198, Footnote *b*).

Experimental.

The tabulated data given are representative of results obtained by the authors in operations carried out on control and commercial mixtures substantially in accordance with the methods outlined above. A slight variation from the prescribed procedure should, however, be noted in the second series, namely, that a 5 per cent sodium hydroxide solution was employed in effecting hydrolysis; likewise, in the fourth series, where two 30 cc. and one 20 cc. portions of chloroform were used in the recovery of phenacetin.

Series 5 and 6 involve a commercial preparation in tablet form alleged to contain 2·5 grains (0·1620 grm.) each of phenacetin and salol.—*Journal of Industrial and Engineering Chemistry*, vii., No. 8.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF COPPER AND IRON IN PIG LEAD, LEAD OXIDES, AND LEAD CARBONATE.

By BERNARD S. WHITE.

MOST methods in use for the determination of the small percentage of copper contained in pig lead, lead oxides, and lead carbonate are long and tedious. This is especially true in those instances where refined metal serves as the base for the finished product and the copper content being extremely low, many difficulties present themselves; these can be overcome by the use of this colorimetric method.

While the estimation of the iron content in these compounds can be readily carried out colorimetrically by a separate analysis (*Journ. Ind. Eng. Chem.*, 1912, iv., 659), it has been found that the following method, which combines the determination of both copper and iron colorimetrically in one analysis, adds greatly to the rapidity and accuracy in finding the percentages of these impurities.

Table I.—*Comparative Results* (*Percentages* Cu) *by Fresenius, and Author's Colorimetric Method.*

No.	Pig lead.		Litharge and red lead.		$CuSO_4$ solution.		
	Fresenius.	Colour.	Fresenius.	Colour.	Fresenius.	Colour.	Per cent Cu present.
1.	0·0009	0·00088	0·002	0·002	0·002	0·002	0·002
2.	0·0013	0·0013	0·0008	0·0008	0·0008	0·0008	0·0008
3.	0·0009	0·00088	0·0009	0·00088	0·00066	0·00066	0·0007
4.	0·002	0·002	0·0007	0·0007	0·001	0·001	0·001
5.	0·001	0·001	0·0015	0·0015	0·00066	0·00066	0·00066
6.	0·0015	0·0015	0·0038	0·0038	0·0015	0·0015	0·0015
7.	0·0012	0·0012	0·00088	0·00088	0·00088	0·00088	0·00088
8.	0·0079	0·0079	0·00088	0·0009	0·0009	0·00088	0·0009
9.	0·0013	0·0013	0·0013	0·0013	0·0015	0·0015	0·0015
10.	0·0004	0·0004	0·00066	0·00066	0·0007	0·00066	0·0007

The method not only eliminates the use of hydrogen sulphide, but it shortens the time of a single analysis to thirty or forty minutes, while the results attain the same degree of accuracy as those established by the longer and more complicated methods.

The method of procedure varies somewhat with the nature of the sample to be examined; hence, it will be necessary to make especial mention of red lead.

Analysis of Pig Lead, Litharge, and Lead Carbonate.

Weight of Sample.—In analysing refined pig lead, or lead compounds made from refined metal, it is necessary, owing to the small percentages of copper and iron usually present, to use large samples. It has been found, by the use of this method, that smaller samples may be used with equally accurate results, thereby reducing the bulk to be handled and eliminating any errors which frequently result from the use of large volumes. A sample weighing 30 grms. has been found sufficiently large for refined products, and not over 10 grms. need be used for the crude or unrefined material.

Method of Procedure.—Weigh the finely-divided sample in a 400 ec. beaker, and add small portions of hot (1 : 1) nitric acid until solution is effected. If any basic lead nitrate has been formed, dilute slightly with warm water, and boil. Add 32 cc. (1 : 1) sulphuric acid, stirring constantly while adding. Let the precipitate settle, and decant filtrate through a coarse filter-paper. Wash four times by decantation, using four portions of warm distilled water. Transfer the precipitate to the paper, wash again, and allow to drain. Make the filtrate neutral with ammonium hydroxide, and add 4 cc. excess. Boil for a short time, and filter. Wash the precipitate well with warm water, and reserve for the determination of the iron. Render the filtrate acid with special C. P. hydrochloric acid, adding not more than two drops excess. Add six drops of (1 : 10) potassium ferricyanide solution, filter through close filter-papers using two to each funnel. Catch the filtrate and inspect for copper ferrocyanide. Let the precipitate drain well without washing. Dissolve the copper ferrocyanide off of the paper with alternate washings of small portions of ammonium hydroxide and hot water. Wash well, and keep the bulk to 30 or 40 cc. Render slightly acid with hydrochloric acid, adding not over two drops excess. Transfer to a 100 cc. Nessler tube, and dilute to mark with distilled water. The copper is then determined colorimetrically according to a modification of the method of Carnelly (Sutton's "Volumetric Analysis," p. 204).

In another Nessler tube place 10 cc. dilute ammonium chloride solution, two drops concentrated hydrochloric acid and 90 cc. distilled water, add, from a burette graduated to tenths of 1 cc., standard copper sulphate solution until the colour matches the sample under examination.

Standard Copper Sulphate Solution (Sutton's "Volumetric Analysis," p. 205).—"Dissolve 0·393 grm. of pure $CuSO_4.5H_2O$, in 1 litre of distilled water. One cc. = 0·0001 grm. copper," or 0·00033 per cent when using a 30 grm. sample.

Analysis of Red Lead.

Treat 30 grms. of the sample with 40 cc. (1 : 1) nitric acid, using great care that the violence of the reaction does not cause the sample to froth over the beaker. Slowly add 30 to 40 cc. of 3 per cent hydrogen peroxide, stirring constantly. Boil until solution is effected, and proceed as directed under the "Analysis of Pig Lead."

Sodium sulphite C. P. may be used in place of the hydrogen peroxide, for effecting the solution of lead peroxide, adding it dry in small portions, and boiling until no brown lead peroxide is present.

Determination of Iron in the above Compounds.

For the iron determination use the precipitate of iron hydroxide removed from the copper solution, proceeding as follows:—Dissolve the precipitate contained on the paper with (1 : 1) hydrochloric acid, collecting the filtrate in a 300 cc. volumetric flask. Wash the paper free from acid with hot distilled water, dilute to mark, and mix thoroughly. Place 10 cc. in a 100 cc. Nessler tube, add three drops nitric acid, 10 cc. (1 : 15) ammonium sulphocyanide solution, dilute to mark, and compare with a standard iron solution according to the method outlined by Schaeffer (*Journ. Ind. Eng. Chem.*, 1912, iv., 659):—

"The colour is compared with a blank made in the following manner: A solution of ferric ammonium sulphate of known strength is required. This is made by dissolving 0·7022 grm. of ferrous ammonium sulphate in water. Acidify with sulphuric acid, heat to boiling, and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink colour tends to vitiate the results. Allow the solution to cool, and dilute to 1 litre. One cc. of this solution equals 0·0001 grm. of iron.

"Prepare the blank by pouring into a 100 cc. Nessler cylinder, 10 cc. ammonium sulphocyanide solution, and three drops of concentrated nitric acid. Dilute to 100 cc., and titrate to the exact colour developed in the sample under examination, by the addition of the standard ferric ammonium sulphate solution. One cc. of this solution equals 0·01 per cent iron as the 10 cc removed from the flask contained 1 grm. sample. It will be found that the colour can be accurately compared to within 0·001 per cent of iron content."

Comparison of Results on Copper.

Table I. shows the results obtained by the above method, as compared with the method set forth by Fresenius ("Quantitative Chemical Analysis," ii., 584), on two sets of samples and a copper sulphate solution of known strength.

Precautions and Interfering Elements.

If the sample contains much zinc the following method may be used for removing it:—The filtrate from the iron precipitation, before precipitating the copper ferrocyanide, is rendered slightly acid with acetic acid, and 5 cc. of an 8 per cent sodium ammonium phosphate solution are added; boil, cool, filter, and treat the filtrate as before outlined.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the colorimetric comparison of copper. If a faint white cloud of lead ferrocyanide should develop in the sample under examination, the addition of a small amount of very dilute lead nitrate solution to the standard will overcome this difficulty.

Reagents and Indicators.—This method presupposes the use of absolutely pure reagents, especially free from iron and copper. Use litmus paper as an indicator, as all other indicators, once introduced, will affect the final colour.—*Journal of Industrial and Engineering Chemistry*, vii., No. 12.

THE PRODUCTION OF AROMATIC HYDROCARBONS FROM PARAFFIN WAX.

By GUSTAV EGLOFF and THOMAS J. TWOMEY.

The cracking of paraffin wax into lower boiling hydrocarbons has been made a study of in a number sf investigations which are widely quoted. The first workers in this field were Thorpe and Young (*Liebig's Ann.*, clxv., 28; Chem. News, 1871, xxiii., 174), who cracked paraffin wax by distillation under pressure. In the distillate there was identified pentane, hexane, heptane, octane, nonane, probably also decane and undecane, as well as amylene, hexylene, &c., up to nonylene. Gawalowski (*Oesterr. Chem. Tech. Zeit.*, 1910, lxx.) has found recently that paraffin wax (m.p. 45° C.) by prolonged heating in an autoclave may be decomposed into gaseous and liquid products which in both cases are said to belong io the ethylene and acetylene series. At any rate the decomposition oils contain also methane and homologues, cyclical saturated (naphthenes), and unsaturated hydrocarbons. Brooks and co-workers (*Journ. Ind. Eng. Chem.*, 1915, vii., 180; *Journ. Franklin Inst.*, 1915, clxxx., 653; *Journ. Am. Chem. Soc.*, 1916, xxxviii., 393) cracked pure commercial paraffin wax at temperatures not exceeding 420° C. and under 100 lbs. pressure, thus obtaining gasolene entirely aliphatic in composition. The phenomena of the decomposition of wax is also very familiar to those persons who have distilled crude petroleum as well as to the refiners of the oil. The cracking of paraffin wax in the oil takes place usually between 300 and 400° C. under ordinary conditions of distillation at atmospheric pressure. These conditions do not produce such extensive cracking as distillation under pressure and only yield increased amounts of kerosene and not an appreciable amount of gasolene.

There is found nowhere in the literature that aromatic hydrocarbons such as benzene, toluene, and xylenes have been produced in the decomposition of pure paraffin wax. The products of the reaction were also found to be those of the aliphatic group. Special effort to find aromatic compounds, especially by Brooks and co-workers (*loc. cit.*), showed that they were not produced by distillation under 100 lbs. pressure and 420° C.

In view of these results and the development of cracking processes for the production of benzene and toluene from petroleum at the present day, the question has arisen whether or not oils containing paraffin wax are suited for the production of benzene and toluene. That such oils are adapted for gasolene formation is universally accepted. If oils containing paraffin wax are to be used it should be known if the wax is desirable, otherwise the wax should be removed.

The authors saw no apparent reason why benzene and toluene should not be formed when paraffin wax is cracked, provided the proper conditions for the formation reaction were obtained. It was realised that the decomposition of paraffin wax by distillation under pressure as conducted by other investigators would produce only aliphatic compounds, since the proper conditions were not obtainable by this method. It was also recognised that other investigators were seriously handicapped by using this liquid-gas phase method of cracking, which automatically fixes both conditions of temperature and pressure, as is well known from the laws of physical chemistry.

From a study (Rittman, *Journ. Ind. Eng. Chem.*, 1915, vii., 945) of the kinetics of the decomposition of the paraffin series it is indicated that decomposition of paraffin wax would tend toward the formation of aromatic hydrocarbons such as benzene, toluene, and xylene. The formation was also foreseen by Kramer and Bottcher (*Ber. Deutsch. Chem. Ges.*, 1887, xx., 694). In commenting on the work of Thorpe and Young they stated that if a higher temperature had been used the higher boiling olefins would have changed into benzene hydrocarbons but not naphthenes.

For this reason the cracking of paraffin wax by the gas phase method—that is, the cracking of paraffin wax by passing through a heated tube—was undertaken to confirm the authors' opinion that it is possible to form benzene, toluene, and xylenes from paraffin wax under similar conditions which result in the formation of the same compounds from petroleum cracking. As might be expected, positive data to this effect were obtained. The results are interesting in that they show (1) that oils containing paraffin wax are adapted for the production of aromatic hydrocarbons as far as the wax is concerned, (2) that there is a close relationship between the members of the aliphatic and aromatic series of hydrocarbons, (3) that the production of aromatic hydrocarbons formed by the cracking of petroleum may not be ascribed entirely to the presence of compounds in the petroleum containing the phenyl radicle, and (4) the advantage of cracking in the gas phase system for the obtaining of desired results.

For the experiments pure commercial paraffin wax (m.p. 47° C. and containing 0·05 per cent of oil, was used. It was cracked by passing through a heated tube in an apparatus which has been described in detail in other articles (Rittman, *Journ. Ind. Eng. Chem.*, 1914, vi., 472). The wax was melted and placed in the lubricator in this condition. It was kept in this state by heating the lubricator gently with a flame. It was admitted to the cracking area at a constant rate of 246 grms. per hour, a rate of flow which has been used in all of the experimental work on the cracking of oils.

Only two temperatures and pressures were employed—500 and 600° C. and atmospheric and 150 lbs. pressure. The work was undertaken primarily for the purpose of showing that it was possible to produce aromatic hydrocarbons from paraffin wax and not in order to show the effect of temperature and pressure. These effects, in view of the present knowledge of the cracking reaction, may be readily deduced from the results produced by experiments at a few temperatures and pressures.

The accompanying tables show the effect of temperature and pressure on the per cent of recovered oil, the per cent to 170° C. of the recovered oil, with the specific gravities, the distillation with gravities of the cuts of this light oil fraction, and the percentage of benzene, toluene, and xylenes in the recovered oil, as well as on the basis of wax required for the production.

The analysis of the recovered oil was made by means of fractional distillation and specific gravities (Rittman, Twomey, and Egloff, *Met. and Chem. Eng.*, 1915, xiii., 682). However, the benzene, toluene, and xylene formed were also identified by chemical means. The fractions were first deolefinised completely with concentrated sulphuric acid and then nitrated to the mononitro stage. The paraffins associated with the mononitro compounds were separated by dissolving the mixture in concentrated sulphuric acid. A two-layer system resulted—paraffins and a mixture of mononitro compounds and sulphuric acid. The mixture of sulphuric acid and mononitro compounds was then nitrated to the dinitro state. The dinitro compounds were washed free from acid, recrystallised from alcohol, and then identified by means of their melting-point.

Table I.—*The Effect of Temperature and Pressure on the per cent of Recovered Oil.*

Temperature.	Present.	P c recovered.
500° C.	Atmospheric	92·3
600° C.	,,	46·3
500° C.	150 lbs.	78·0
600° C.	150 lbs.	39·7

Table II.—*The Effect of Temperature and Pressure on the Distillate to* 170° C. *and the Specific Gravity.*

Temperature.	Pressure.	P.c. to 170° C.	Specific gravity
500° C.	Atmospheric	0·08	0·723
600° C.	,,	15·40	0·762
500° C.	150 lbs.	12·90	0·753
600° C.	150 lbs.	28·80	0·830

Table III.—*The Effect of Temperature and Pressure on the Specific Gravity and per cent of the Benzene Cut to* 95° C., *on the Specific Gravity of the Toluene Cut* 95° C. *to* 120° C., *and the Specific Gravity of the Xylene Cut* 120° C. *to* 150° C.

Temp.	Pressure.	P.c. to 95°.	Sp. gr.	P.c. 95° to 120 C.	Sp.gr.	P c. 120° to 150°.	Sp.gr.
500° C.	Atmospheric	0·0	—	0·0	—	0 0	—
600° C.	,,	2·96	0·747	3·84	0·768	5·0	0·773
500° C.	150 lbs.	5·80	0·762	3·14	0·788	1 8	0·790
600° C.	150 lbs.	10 60	0·820	7·20	0·835	3·8	0·824

Table IV.—*The Effect of Temperature and Pressure on the per cent of Benzene, Toluene, and Xylene in the Recovered Oil.*

Temperature.	Pressure.	P.c. benzene.	P.c. toluene.	P.c. zylene.
500° C.	Atmospheric	0·0	0·0	0·0
600° C.	,,	0·5	1·0	0·6
500° C.	150 lbs.	1·5	1·3	0·5
600° C.	150 lbs.	6 6	5·4	2·3

Table V.—*The Effect of Temperature and Pressure on the per cent of Benzene, Toluene, and Xylene on the Basis of Paraffin Wax used for their Production.*

Temperature.	Pressure.	P.c. benzene.	P.c. toluene.	P.c. zylene.
500° C.	Atmospheric	0·0	0·0	0·0
600° C.	,,	0·2	0·5	0·3
500° C.	150 lbs.	1·2	1·7	0·4
600° C.	150 lbs.	2·6	2·2	0·9

No attempt was made to distil or analyse the fraction of oil boiling above 170° C., as it was considered that no naphthalene or anthracene was formed.

At atmospheric pressure and 500° C., under the conditions of the experiment, but very little cracking of the paraffin wax took place, and to all appearances what cracking occurred produced members only of the aliphatic series. Under the other conditions which were obtained, benzene, toluene, and xylene, as shown by physical and chemical tests, were formed in appreciable amounts, although contaminated to a large extent by other compounds such as olefins and paraffins. The aromatic formation increased with increase of temperature and pressure. This phenomena is shown by all cracking experiments in the gas phase method.

The temperatures and pressures used in these experiments do not necessarily represent the critical temperatures and pressures for the formation of aromatic hydrocarbons from paraffin wax. They represent only a few of the many conditions possible for production. Due to the rate at which the paraffin wax was admitted to the tube, it did not necessarily reach equilibrium. With a lower rate of feed conditions approaching the true equilibrium would have been obtained, and in this way data would have been obtained from which the absolute conditions of temperature and pressure required for the formation might have been deduced. At the present time we are not so intensely interested in this side of the question. Hence a rate was employed which has been made the standard for a comparative study of oils.

Compared to a distillate oil boiling between 250 and 350° C. derived from Pennsylvania petroleum the paraffin wax is not so stable and does not produce as much benzene, toluene, and xylene. No explanation is offered at the present time.

The results of this paper may be summarised as follows:—

1. It is possible to produce benzene, toluene, and xylene by the cracking of paraffin wax at 600° C. and atmospheric pressure, and at 500 and 600° C. and 150 lbs. pressure.

2. Under the same conditions of cracking aromatic hydrocarbons also result from petroleum oils of the paraffin type.

3. That the formation of aromatic hydrocarbons produced by the cracking of petroleum may not be ascribed entirely to the decomposition of the constituents of the petroleum which contain the phenyl group.

4. That there is a very close relationship between the members of aliphatic and aromatic series of hydrocarbons.

5. That oils containing paraffin wax are adapted for the commercial production of benzene and toluene.—*Journal of Physical Chemistry*, xx., No. 6.

THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

(Sixth Communication).*

By LEROY McMASTER and A. C. MAGILL.

This work is a continuation of the work which has been in progress in our laboratory for several years on the preparation and investigation of the properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts previously studied were prepared by passing dry ammonia into solutions of the acids in the anhydrous solvents, methyl alcohol, ethyl alcohol, ether, acetone, and benzene, or in mixtures of some of these solvents. In this work we have made use of these same solvents, except methyl alcohol, and in addition we have used pure ethyl acetate. Naumann (*Ber.*, 1910, xliii., 313) found that a great many ammonium salts of organic acids are insoluble in ethyl acetate. Bateman and Conrad (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2553) have recently found that the ammonium salts of some of the halogenoacetic acids are soluble in this reagent. In view of these facts, we thought it would be of interest to attempt to prepare some of the neutral ammonium salts in ethyl acetate. Several of the salts to be described were thus prepared. We have also tested the solubility of some of the ammonium salts in this solvent.

In the following work the neutral ammonium salts of tribromoacetic, phenylbromoacetic, *o*-nitrophenylacetic, phenylamidoacetic, glycolic, α-bromopropionic, β-iodopropionic, β-chlorolactic, trichlorobutyric, caprylic, capric, lauric, myristic, α-bromopalmitic, α-bromostearic, acrylic, β-chlorocrotonic, erucic, dimethylmalonic, dipropylmalonic, isopropylmalonic, butylmalonic, allylmalonic, benzylmalonic, monobromosuccinic, dibromosuccinic, suberic and chlorofumaric acids have been prepared by passing dry ammonia into solutions of the respective organic acids in the above anhydrous solvents. A number of the properties of the salts were studied. The salts were quickly filtered by suction on alundum crucibles, washed with anhydrous ether, tested for neutrality, transferred to crystallising dishes and placed for a short time in a vacuum desiccator.

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* For previous papers on this subject see Chem. News, 1913, cviii., 136; 1913, cviii., 182, 193; 1914, cx., 212; 1914, cx., 224; 1915, cxii., 187. From the *Journal of the American Chemical Society*, xxxviii., No. 9.

The analysis of the salts consisted in determining the nitrogen by the Kjeldahl method. In all the salts except the phenylamidoacetate, the nitrogen present as "ammonium" nitrogen was determined, which is equal to the total nitrogen, except for the phenylamidoacetate and the *o*-nitrophenylacetate. In the case of these two salts, total nitrogen was also determined.

The Substituted Acetic Acids.

Ammonium Tribromoacetate.—Schäffer (*Ber.*, 1871, iv., 371) has prepared and investigated the properties of many of the salts of tribromoacetic acid, but did not prepare the ammonium salt. No reference to this salt can be found in the literature. When ammonia was passed into an ether solution of the acid the salt was precipitated as glistening white leaflets, soluble in water, methyl alcohol, ethyl alcohol, and ethyl acetate. It is insoluble in ether, chloroform, acetone, and benzene. A solution of the salt in water is neutral. The salt is not hygroscopic, and does not give off ammonia in dry or moist air. It decomposes rapidly, with evolution of ammonia, on heating to 50° and completely volatilises below 100°.

This salt can also be prepared by saturating an alcoholic solution of the acid with ammonia and then adding an equal volume of ether. It has the same crystalline appearance as when it is prepared in ether alone.

Calc. for $CBr_3CO_2(NH_4)$:— 4·96 per cent. Found :—4·96 per cent N.

There is a close resemblance in properties between ammonium tribromoacetate and ammonium monobromoacetate prepared by Bateman and Conrad (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2553). Both salts crystallise in white leaflets from alcohol, and are soluble in water and ethyl acetate, and insoluble in benzene. The aqueous solution of the monobromo salt slowly hydrolyses, while the solution of the tribromo salt does not hydrolyse. Neither salt is deliquescent and both are stable in the air. Both salts decompose on warming.

Ammonium Phenylbromoacetate.—There is no record of this salt having been prepared, even by the method of neutralisation of an aqueous solution of the acid. It can be prepared in ether or ethyl alcohol. When prepared in ether it appears as a white amorphous powder, while it is formed as a crystalline compound in ethyl alcohol. The salt is somewhat hygroscopic and is very soluble in water. The solution, which is neutral at first, rapidly hydrolyses. It decomposes rapidly in both dry and moist air, and when heated to 50° it decomposes very quickly, ammonia being evolved. The aqueous solution on being mixed with a solution of lead acetate slowly forms a white crystalline precipitate. The neutral ammonium salt is soluble in methyl alcohol, acetic acid, and an excess of ethyl alcohol. It is very slightly soluble in acetone, and insoluble in ether and benzene.

Calc. for $C_6H_5CHBrCO_2(NH_4)$:—6·06 per cent. Found :—6·02 per cent N.

Ammonium o-Nitrophenylacetate.—No reference to this salt can be found in the literature. It readily precipitates from an ether solution in the form of pale yellow crystals. On account of its solubility in ethyl alcohol, it cannot be prepared in this medium; but if an alcoholic ammonia solution of the acid is added to a large amount of ether, the ammonium salt separates in yellow crystals. This salt was also prepared in acetone and in ethyl acetate in the form of yellow crystals. It is only very slightly soluble in these reagents, but is very soluble in water, methyl and ethyl alcohols, and acetic acid. It is insoluble in benzene and chloroform. The salt is not deliquescent and does not become acid in an aqueous solution which stood for twenty-four hours. It is stable in dry and moist air. It does not decompose at 50° but loses ammonia slowly when heated to 100°.

Both the total and the ammonium nitrogen were determined in this salt, and analyses of the salt prepared in the different solvents proved that we had the neutral salt.

Calc. for $C_6H_4NO_2CH_2CO_2(NH_4)$:—7·07 per cent ammonium N. Found :—7·04 per cent (ether); 7·03 per cent (ethyl alc.); 7·06 per cent (acetone); 7·02 per cent (ethyl acetate).

Calc. for $C_8H_{10}N_2O_4$:—14·14 per cent total N. Found :—14·10 per cent (ether); 14·05 per cent (ethyl acetate).

Ammonium Phenylamidoacetate.—Phenylamidoacetic acid is insoluble in ethyl alcohol, ether, benzene, ethyl acetate, and acetone, but is soluble in water. While our line of work is mainly to prepare the ammonium salts in anhydrous organic solvents, nevertheless we attempted to prepare this compound in aqueous solution since the free acid is insoluble in the above reagents. Furthermore, we could find no reference to the salt having been prepared.

An aqueous solution of the acid was saturated with ammonia and the solution was allowed to evaporate to dryness. Several attempts were made to prepare the neutral salt by this method, but we obtained an acid salt in each case. This was to be expected, as most of the ammonium salts of the organic acids, when thus prepared, are the acid salts and not the neutral salts. Attention has been called to this fact in the introductory statements of the previous papers on this work (*loc cit.*).

The neutral ammonium salt of phenylamidoacetic acid however, was prepared by treating an alcoholic suspension of the acid with dry ammonia. Under this condition, the acid gradually passed into solution. Ether was then added to this solution and there was precipitated a salt in the form of a pale greenish grey powder. It was filtered, washed, and dried in the usual way. Although the free acid is odourless, the salt thus prepared has a slight odour which is very disagreeable.

The salt is very soluble in water and benzene. It is somewhat soluble in methyl alcohol, ethyl alcohol, ethyl acetate, and acetic acid. It is very slightly soluble in acetone, and insoluble in ether and chloroform. The salt can be crystallised from benzene in splendid monoclinic crystals. The aqueous solution, which is neutral at first, slowly hydrolyses and becomes acid. The salt does not lose ammonia in dry or moist air, but it is slightly deliquescent. When warmed to 50° the salt shows no evidence of decomposition, but at 100° ammonia is given off rapidly.

Calc. for $C_6H_5CHNH_2CO_2(NH_4)$:—16·67 per cent. Found :—16·62 per cent total N.

Ammonium Glycolate.—Heintz (*Jahresb. Fortschr. Chem.*, 1861, p. 446) mentions the acid ammonium salt of glycolic acid and states that it crystallises as fine needles, which are easily soluble in water and hot alcohol. Ssabanejew (*Chem. Zentr.*, 1899, II., xxxii.) describes the preparation of a neutral solution of ammonium glycolate by treating a solution of glycolic acid with the calculated amount of ammonia. The experiment was carried out in a vacuum. On evaporation of the solution, there was obtained the acid salt in needle-like crystals. The literature contains no mention of the preparation of the neutral salt by precipitation.

On passing ammonia into a dilute solution of the acid in ethyl alcohol, a white precipitate of the ammonium salt at first appeared, which soon went into solution since this salt is quite soluble in alcohol. On continuing the addition of the ammonia, heat was developed and no further precipitate formed. The alcoholic solution was allowed to evaporate in the air and there was formed a syrupy liquid and some fan-like crystals. This experiment was epeated several times. The syrupy liquid was found to distil at but a few degrees below the boiling point of pure ethyl glycolate. The liquid was evidently a mixture of the ethyl ester of glycolic acid and ammonium salts of the acid.

Results similar to this have been previously noticed by one of us (McMaster, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1923) and by Bateman and Conrad (*loc. cit.*). Heat favours the formation of the esters, and attention was called to the fact in a previous paper on this subject that, when the experiments are carried out in ethyl alcohol, it is necessary to keep the flasks surrounded by cold water, for, when the ammonia is passed into the solution of the acid in alcohol, heat is set free due to the action of the ammonia on the alcohol and also to the heat of neutralisation. While in most of our experiments the precipitation flasks have been kept cold when the alcohols were used as solvents for the organic acids, in this case the flask was not kept cold. No doubt that in many of the cases, where the ammonium salts of even fairly strong acids were being prepared in the alcohols and the mixtures kept cold, small amounts of esters were formed. They were removed by excess of alcohol and by the ether used to wash the salts while in the alundum crucible.

However, when a very concentrated alcoholic solution of the glycolic acid was usod, the precipitate which formed at first was not redissolved and very little ester was formed. The most of the acid was converted into the ammonium salt, and the limit of the solubility of this salt in the alcohol present was reached. The salt formed in small salt like crystals. When recrystallised from alcohol they appeared in the form of needles.

When dry ammonia was passed into a solution of the acid in acetone much heat was evolved and a fine white precipitate formed, which almost immediately dissolved to form a brown solution. Owing to the heat evolved we suspected the formation of some diacetoamine by the action of ammonia on the acetone vapour present. In order to determine whether this was true we prepared some diacetoamine by passing ammonia and acetone vapour together through a tube heated to 100°. This is the method used by Heintz to prepare diacetoamine (*Ann.*, 1874, clxxiv., 133). To the diacetoamine was added an acetone solution of glycolic acid. Fine white crystals were formed which were insoluble in an excess of the diacetoamine. They were presumably a salt (Heintz, *Ibid.*, 1879, cxcviii., 42; 1880, cciii., 336), formed by the action of the basic amine on the acid. If the diacetoamine is saturated with ammonia before adding the acid white crystals form, but almost immediately redissolve and form a brown solution. If some dry neutral ammonium glycolate (preparation of which will be described later) is added to diacetoamine it readily dissolves and forms the brown solution. From these reactions we have concluded that the white crystals which formed when the ammonia was passed into an acetone solution of the acid, and which dissolved almost at once to form a brown solution, consisted of the neutral ammonium salt, soluble in the diacetoamine produced during the experiment as a result of the action of ammonia gas on the vapour of the acetone and the mixture becoming hot. While neutral ammonium salts of the organic acids have been previously prepared in acetone by one of us (McMaster), the formation of diacetoamine has not been encountered. The reason for this is probably due to the fact that the solutions were kept cool during the passing in of the ammonia or that the heat of reaction was not so great as in this case. In fact we repeated the experiment, and kept the acetone solution of the glycolic acid cold while passing in the ammonia. No diacetoamine was formed, but it was found necessary to agitate the cold acetone solution of the acid in an atmosphere of ammonia for several hours in order to obtain a yield of the ammonium salt. The salt separated out as fine white crystals and analysis proved it to be the neutral ammonium salt.

When ammonia was passed into a solution of the acid in benzene coarse large crystals formed. Analysis of these crystals showed that they were a mixture of the acid salt and the neutral salt. No further attempt was made to prepare the neutral salt in benzene.

The neutral ammonium salt can be easily prepared in an ethyl acetate solution of the acid. It precipitated as fine white crystals, very soluble in water. The aqueous solution gives a neutral reaction, but soon becomes acid, due to hydrolysis. The salt is also very soluble in methyl alcohol, acetic acid, and diacetoamine. It is slightly soluble in ethyl alcohol and ether and insoluble in ethyl acetate, chloroform, benzene, and acetone. It decomposes slowly in dry air and very rapidly in moist air, giving off ammonia. It is also slightly hygroscopic. On warming to 50° decomposition of the salt took place rapidly, and at 100° the salt was completely decomposed into ammonia and the acid.

> Calc. for $CH_2OHCO_2(NH_4)$:—15·05 per cent N.
> Found :—15·03 per cent (ethyl acetate); 15·01 per cent (acetone).

Comparison of Results.—The ammonium salt of phenylacetic acid has been prepared and described in a previous paper by one of us (McMaster, *loc. cit.*). A comparison of the salts of phenylacetic acid and its substituted derivatives shows many points of similarity. They can all be prepared in alcohol, although phenylamidoacetic acid is insoluble in this medium. The salts of *o*-nitrophenylacetic acid and phenylamidoacetic acid are yellowish in colour. The others are white. They are all soluble in water and slightly soluble in acetone, but insoluble in ether and benzene. The phenylbromoacetate and phenylamidoacetate are slightly deliquescent, while the others are not deliquescent. The phenylacetate and phenylbromoacetate give off ammonia slowly in moist air. The others do not give off ammonia in the air.

Ammonium glycolate (hydroxyacetate) is quite unlike the salts of the other substituted acetic acids. It is insoluble in acetone and slightly soluble in ethyl alcohol and ether. It is also insoluble in ethyl acetate, benzene, and chloroform. It loses ammonia very rapidly in most air. Like the phenylbromoacetate and phenylamidoacetate it is slightly hygroscopic.

The Substituted Propionic Acids.

Ammonium α-Bromopropionate.—Weinig (*Ann.*, 1894, cclxxx., 248) has investigated the properties of many of the metallic salts of α-bromopropionic acid but does not mention the ammonium salt. It can be easily prepared by treating an ether solution of the acid with ammonia. The heat of reaction is so great that in order to prevent possible decomposition of the salt the precipitation flask must be packed in ice. The salt separates out as a non-crystalline powder. The salt is quite soluble in ethyl alcohol, and in order to prepare it in this medium it is necessary to saturate the alcoholic solution of the acid with ammonia and pour it into a large amount of ether. Under these conditions the salt forms as large flaky crystals instead of an amorphous powder, as is the case when it is prepared in the ether direct. The salt is also very soluble in methyl alcohol, acetic acid, and water. The neutral aqueous solution slowly becomes acid. The salt is slightly deliquescent. It is stable in dry air but loses its ammonia slowly in a moist atmosphere. It is insoluble in ethyl acetate, chloroform, acetone, and benzene. It does not decompose at 50° in dry air, but at 100° ammonia is given off slowly.

> Calc. for $CH_3CHBrCO_2(NH_4)$:—8·23 per cent.
> Found :—8·21 per cent N (ether); 8·21 per cent N (ethyl alcohol).

Ammonium β Iodopropionate.—The literature contains no account of this salt. By our method it formed in ether in frost-like crystals, which gradually became amorphous. It can also be precipitated in the crystalline condition from a concentrated solution of the acid in ethyl alcohol. The salt is slightly deliquescent and readily soluble in water, forming a neutral solution which slowly becomes acid. It is quite soluble in methyl and ethyl alcohols, acetic acid and acetone, slightly soluble in chloroform, ether, and ethyl acetate. It is insoluble in benzene. Upon standing several months the salt becomes brown, due to liberated iodine. A rancid odour also developed.

The salt does not lose ammonia in dry air, but does so very slowly in moist air. At 50° there is no evidence of ammonia being given off, but at 100° the salt decomposes slowly.

Calc. for $CH_2ICH_2CO_2(NH_4)$:—6·45 per cent. Found:—6·45 per cent N.

Ammonium β-Chlorolactate.—This salt can be prepared from a solution of the acid in either ethyl alcohol or ether. In the alcohol the salt forms as small white crystals and in the ether as a granular powder. It is not deliquescent, is stable in dry air, and readily gives off ammonia in moist air. It gives off ammonia slowly at 50° and somewhat more rapidly at 100°.

The salt is very soluble in acetic acid and water. The neutral aqueous solution soon becomes acid. Silver nitrate gives a white precipitate when added to an aqueous solution of this salt. The precipitate is soluble in ammonium hydroxide. The salt is very slightly soluble in methyl alcohol and ethyl alcohol, and insoluble in ether, chloroform, acetone, benzene, and ethyl acetate. No mention of this salt can be found in the literature, although many of the other salts of β-chloroacetic acid have been studied.

Calc. for $CH_2ClCH(OH)CO_2(NH_4)$:—9·89 per cent N. Found:—9·85 per cent (ether); 9·87 per cent (ethyl alcohol).

Comparison of Results.—The neutral ammonium salts of propionic acid (*Am. Chem. Journ.*, 1913, xlix., 299) and its substituted derivatives thus far studied can be prepared in ether, from which they separate as amorphous solids. The β-iodopropionate and β-chlorolactate can be precipitated as white crystals from concentrated alcoholic solutions of the acids. The β-chlorolactate is slightly soluble in ethyl and methyl alcohols. The other ammonium propionates are readily soluble in these solvents. All of them are very soluble in water and acetic acid and insoluble in benzene. They are unstable in moist air, losing ammonia rapidly. The β-chlorolactate is not deliquescent while the others are.

Some Higher Fatty Acids, including several Substituted Derivatives.

Ammonium Trichlorobutyrate. — Garzarolli Thurnlak (*Ann.*, 1876, clxxxii., 185) prepared this salt by treating an ether solution of the acid with solid ammonium carbonate. The ether was evaporated from this mixture by means of a stream of dry air. The salt was then extracted from the residue by means of more ether. It crystallised out of water partly in tuft-like and partly in quartz-like crystals. The salt was found to be more readily soluble in water and alcohol than in ether.

We prepared this salt in ether by our usual method. It formed as a white amorphous solid. It is very soluble in ethyl alcohol, and on this account the yield is small if the ammonia is conducted even into a saturated alcoholic solution of the acid. It can be prepared also by passing ammonia into a saturated solution of the acid in acetone or ethyl acetate and then adding a large amount of ether. In each solvent the precipitate formed was crystalline. It dissolved readily in water, the solution remaining neutral for at least several days. The salt is also very soluble in methyl alcohol, and appreciably so in ethyl acetate and acetone, and very slightly soluble in chloroform and ether. It is insoluble in benzene. It is not hygroscopic.

At ordinary temperatures the salt is stable in dry air, but at 50° ammonia is rapidly given off. Ammonia is given off slowly in moist air at room temperature. When heated to 100° the salt decomposes into the acid and ammonia.

Calc. for $C_3H_4Cl_3CO_2(NH_4)$:—6·73 per cent N. Found:—6·70 per cent (ether).

Ammonium butyrate has been described in one of the papers previously referred to. Ammonium trichlorobutyrate undergoes decomposition into ammonia and the acid salt very slowly in the air, while ammonium butyrate does so very rapidly. The aqueous solution of the latter hydrolyses very rapidly while that of the former does so very slowly. Both the butyrate and the trichlorobutyrate are easily precipitated from ether solutions of the acids, the first one in the form of granular crystals and the second one as an amorphous powder. Both are soluble in the alcohols, acetic acid, and acetone. Ammonium isobutyrate, also described in a previous paper, precipitates from an ether solution of the acid as a lustrous white solid, and differs from the butyrate and the trichlorobutyrate in that it has a very high vapour tension. The ammonium butyrate is deliquescent, while the isobutyrate and the trichlorobutyrate are not deliquescent. The ammonium isobutyrate resembles the other two as to solubility in the alcohols.

Ammonium Caprylate.—Currie (*Journ. Agr. Research*, 1914, ii., 8) found that he could prepare this salt by passing dry ammonia into a benzene solution of the acid. He obtained needle-like crystals, which readily hydrolysed in an aqueous solution, and which readily gave off the odour of caprylic acid when exposed to the air. No analysis of the salt was recorded by Currie. We have prepared the salt in ether. It dried to a cheese-like mass. It did not precipitate from ethyl alcohol, but when a mixture of equal parts of ether and alcohol were used it precipitated as monoclinic crystals. An aqueous solution of the salt lathers freely on shaking. This solution, which is neutral at first, becomes acid on standing a very short time. The salt is slightly hygroscopic, loses ammonia very slowly in dry air and very rapidly in moist air. It is very soluble in acetic acid and ethyl alcohol, and slightly soluble in methyl alcohol. It is less soluble in acetone and ethyl acetate than in methyl alcohol. It is insoluble in chloroform, ether, and benzene. Analysis of the salt dried at 50° showed that there had been some decomposition.

Calc. for $C_7H_{15}CO_2(NH_4)$:—8·70 per cent N. Found:—8·68 per cent (ether); 8·64 per cent (alcohol-ether mixture).

After standing some weeks the above salt became yellowish in colour and developed the odour of caprylic acid.

Ammonium Caprate.—Currie (*loc. cit.*) also describes the preparation of this salt in benzene, and found that its properties are the same as those of ammonium caprylate. The salt can also be prepared in ether as a fine white amorphous substance which is greasy to the touch. By conducting ammonia into a saturated alcoholic solution of the acid and then adding an excess of ether, the neutral salt precipitates as fine white crystals. It dissolves readily in water, to which it imparts a neutral reaction. The solution quickly hydrolyses. The salt is slightly hygroscopic. It is insoluble in benzene, slightly soluble in acetone and ether, and readily soluble in methyl alcohol, ethyl alcohol, and acetic acid. It gives off ammonia slowly in dry air and rapidly in moist air. At 50° the evolution of ammonia is very rapid and is complete before the temperature reaches 100°.

Calc. for $C_9H_{19}CO_2(NH_4)$:—7·41 per cent. Found:—7·41 per cent N.

Ammonium Laurate.—Many of the salts of lauric acid have been prepared by Oudemans (*Jahr. Fortschr. Chem.*, 1863, p. 331), who prepared the acid ammonium salt by neutralising an aqueous solution of the acid with ammonium hydroxide and evaporating to crystallisation.

When the dry ammonia was passed into an ether solution of the acid there was formed a curdy white precipitate, which soon changed to one flaky in appearance. It was also prepared by adding ether to an alcoholic ammonia solution of the acid. In this case fine white crystals formed. The salt is very soluble in water. This aqueous solution remains neutral for at least two days. It also lathers very freely when shaken. The salt is soluble in methyl and ethyl alcohols and acetate acid, slightly soluble in acetone, and insoluble in chloroform, ether, and benzene. The salt is deliquescent. It does not lose ammonia in exposure to dry or moist air. It gives off ammonia slowly at 50° and decomposes very rapidly at 100°.

Calc. for $O_{11}H_{23}CO_2(NH_4)$:—6·45 per cent N. Found:—6·44 per cent (ether); 6·43 per cent (ether-alcohol mixture).

Ammonium Myristate.—No record can be found of the preparation of this salt. It can be prepared by passing dry ammonia into an ether solution of myristic acid. On passing in the gas there was formed a fine white non-crystalline precipitate. By dissolving this precipitate in ethyl alcohol and evaporating the solvent, the salt was obtained in the crystalline form. It is easily soluble in water, the solution remaining neutral at the end of two days. It is readily soluble in ethyl alcohol, methyl alcohol, and acetic acid, and insoluble in ether, benzene, acetone, and chloroform. It is not hygroscopic. At ordinary temperatures there is no evidence of decomposition in dry air, but it decomposes slowly at 50°, and is completely decomposed at the temperature of boiling water. It decomposes very slowly in moist air.

Calc. for $C_{13}H_{27}CO_2(NH_4)$:—5·71 per cent. Found:—5·70 per cent N.

(To be continued).

NOTICES OF BOOKS.

Raphael Meldola, D.Sc., F.R.S., Reminiscences of his Worth and Work. Edited by James Marchant, with a Preface by the Right Hon. Lord Moulton. London: Williams and Norgate. 1916. Pp. xv. + 225. Price 5s. net.

This little volume of reminiscences may be regarded as a small tribute in affectionate and grateful remembrance of a great scientific man, whose death was a loss which England can ill afford at the present critical moment. Prof. Meldola was universally acknowledged to be a man of entire devotion to the advancement of knowledge and one whose zeal for truth was unsurpassed, and in addition he was possessed of great practical ability and knowledge of the applications of chemistry, as is unanimously pointed out by the writers of this collection of short sketches, who include Professors Dalby, Pope, the late Silvanus P. Thompson, and others. Each one of them has something to say in enthusiastic praise of his character or work, and the whole provides an inspiring and attractive view of his personality. Prof. Arthur Green gives a detailed account of the chemical investigations undertaken by him, and his work in other branches of science is described by equally competent writers.

Fifty-second Annual Report on Alkali, &c., Works. By the Chief Inspector. London: Wyman and Sons, Ltd. 1916. Pp. 100. Price 2s.

In this report the Chief Inspector calls attention to the fact that naturally much work has been done during the year in connection with the manufacture of chemicals used for munitions of war, and many works and processes came under inspection for the first time. In spite of difficulties inspections and tests were carried out very much as usual during the year. The report contains a long and very valuable account of the results obtained in the direct process for the manufacture of ammonium sulphate. In gas works it was frequently found that the method had a deleterious effect upon the oxide of iron purifiers through which the illuminating gas is passed before being conveyed to consumers, and the procedure in some works evidently leaves much to be desired. Some clues were obtained as to the reasons of the unsatisfactory results, which were not by any means universal, some works reporting that the process had been worked continuously for two, three, or even four years without trouble of any kind. The inspector suggests some factors which may affect the results, but in the present state of our knowledge it is not easy to prescribe remedies very definitely.

The Gas Chemists' Summary, 1915. By A. V. Hendrickson. London: Walter King. 1916. Pp. 216. Price 3s. 6d.

This handbook gives a fairly detailed summary of the literature published during 1915 of interest to gas chemists, and is an indispensable possession for those who wish to keep abreast of the times in the easiest possible manner. The author quotes a very large number of authorities, and the bibliography contains 134 titles of books and papers in English, French, and German. In spite of interruptions and difficulties it would appear that a good deal of important work has been done during the year, and the arrangement of the text is such that there should be no difficulty in looking up any particular detail; the addition of a name as well as a subject index is a great advantage. Some interesting results are chronicled relating to work on gas heating and ventilation, and also upon tar testing and the manufacture and analysis of ammonium sulphate.

Analytical Chemistry. Based on the German Text of F. P. Treadwell, Ph.D., translated and revised by William T. Hall, S.B. Volume I.: Qualitative Analysis. Fourth English after the Eighth German Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. xiii. + 538. Price 12s. 6d. net.

The new edition of this work is not a literal translation of Prof. Treadwell's original although based upon it, but contains so much additional matter that it may almost be regarded as a new work. However, all the excellent features of the German book are prominent in it, and no deviation has been made from the general plan. It is undoubtedly in many respects one of the most comprehensive treatises on qualitative analyses extant, and will be found valuable as a work of reference as well as for descriptions of some of the less common processes. The theory of analytical work is treated particularly fully and the law of mass action and the ionic theory are discussed in considerable detail. In the practical parts of the book very delicate and precise methods of estimation are described, and great stress is laid upon the importance of using reagents of known strength and of keeping in mind the quantitative aspects even in qualitative work.

Scientific Papers of the Bureau of Standards. No. 286. Determination of Aluminium as Oxide. By William Blum. Washington: Government Printing Office. 1916. Pp. 20. Gratis on application.

This pamphlet contains an account of the systematic study of the precautions which must be observed in precipitating, weighing, and igniting aluminium hydroxide for the purpose of determining aluminium as oxide. The author found that methyl red and rosolic acid can satisfactorily be employed as indicators to show when precipitation by ammonia is complete, and that the presence of ammonium chloride is an advantage. The precipitate may equally well be washed with ammonium nitrate or ammonium chloride. Owing to the hygroscopicity of aluminium oxide the crucibles containing the ignited precipitate should be kept covered in the desiccator and on the balance. Ignition will be found to be complete in the case of precipitates of Al_2O_3 weighing from 0·1 to 0·2 grm. after from five to ten minutes' exposure to the blowpipe blast.

Conférences de Chimie Minérale faites à la Sorbonne. ("Lectures on Mineral Chemistry given at the Sorbonne"). By MARCEL GUICHARD. Second Edition. Paris: Gauthier-Villars et Cie. 1916. Pp. ix.+422. Price 15 fr.

IN view of the rather astonishing statement made at the beginning of the preface to this book—that there is no book in French dealing with the metals and intended for the use of students in the universities—the publication of it will most certainly be welcomed by both teachers and learners. It contains a fairly full descriptive account of the chemistry of the most important metals; analytical reactions are not usually included, nor is much space given to the consideration of the details of large scale operations or plant. On the other hand, the alloys are treated very fully, and special care is taken to give adequate accounts of the most characteristic compounds of each metal. Some theoretical discussions are included, as seems appropriate and convenient; for example, an excellent short account is given of catalysis and catalytic agents. The work of the skilled teacher is plainly apparent in the book, and the student who works through it will have nothing to unlearn when he advances to the use of larger and more comprehensive works. The author rejects Mendeleeff's classification of the elements as being by no means the best for teaching purposes, but in other respects there is no great novelty of treatment in the text.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 11, September 11, 1916.

Total Destruction of Pentoses in the Course of Alcoholic Fermentation.—H. Pellet.—If 1 or 2 grms. of arabinose or xylose are added to a solution containing 200 grms. of molasses per litre and 5 to 10 grms. of yeast, and the temperature is kept at 28–32°, there is always a loss of pentoses, amounting to 10 to 20 per cent of the quantity originally present, when fermentation is complete; *i.e.*, after forty-eight to sixty hours. By varying the conditions of the experiment it is possible to make this loss of pentoses considerable or even total, or to make the amount fermented negligible. This last is the case when the quantities employed are 50 grms. of yeast in a solution containing 100 grms. of molasses per litre.

No. 12, September 18, 1916.

Action of X-Rays on Iodine and Iodide of Starch in Aqueous Medium.—H. Bordier.—The X-rays readily decolorise iodide of starch, the blue colour reappearing when a trace of iodine is added to the liquid. With iodised water the action of the rays may be observed by adding a little starch to the water after exposure to the rays; it remains colourless, while a control specimen, which has not been exposed to the rays, at once turns blue. The X rays in a few minutes produce the same effect as the ultra-violet rays in several hours; in both cases the electrified particles become discharged and the iodine is no longer in the colloidal state.

MISCELLANEOUS.

Faraday Society.—A General Discussion on "Refractory Materials" will be held on Wednesday, Nov. 8, 1916, from 5.30 to 7 and from 8.30 to 10.30 p.m., at the Institution of Electrical Engineers, Victoria Embankment, W.C. (near Waterloo Bridge). The following are the arrangements:—

Sir Robert Hadfield, F.R.S., President, will take the Chair and will deliver an Introductory Address.

Dr. J. W. Mellor will give the Opening Paper, and will deal principally with "The Texture of Refractories."

Dr. H. G. Colman will speak on the work of the Joint Refractory Materials Committee of the Institution of Gas Engineers and the Society of British Gas Industries.

Mr. Albert Cliff will speak on "The Manufacture and Prospects of Refractories."

Mr. E. P. Page will speak on "The Classification of Refractory Materials and some Notes on Method and Points for Investigation."

Mr. J. Allen Howe will make a statement on "The Recent Work of the Geological Survey on Refractory Materials."

Prof. W. G. Fearnsides will read a paper on "The Application of Petrographic Methods to the Study of Refractory Materials."

Mr. Cosmo Johns will read a paper on "Silica as a Refractory Material."

Dr. P. G. H. Boswell will speak on "Refractory Sands."

Mr. Ezer Griffiths, M.Sc., will read a paper on "The Transmission of Heat through Materials Employed in Furnace Construction."

Mr. F. W. Harbord, Prof. J. W. Cobb, Dr. W. Rosenhain, F.R.S., Mr. W. C. Hancock will also speak, and the subject will then be thrown open for general discussion.

MEETINGS FOR THE WEEK.

TUESDAY, 7th.—Röntgen Society, 8.15. (General Meeting).

WEDNESDAY, 8th.—Faraday Society, 5.30 General Discussion on "Refractory Materials."

THURSDAY, 9th.—Royal Society. "Methods of raising a Low Arterial Pressure," by W. M. Baylis. "Selective Permeability—the Absorption of Phenol and other Solutions by the Seeds of *Hordeum vulgare*," by A. J. Brown and F. Tinker. "Toxic Action of Dilute Pure Sodium Chloride Solutions on the Meningococcus," by C. Shearer. "The rôle of the Phagocyte in Cerebro-spinal Meningitis," by C. Shearer and H. W. Crowe. "Investigations dealing with the Phenomena of 'Clot' Formations—Part IV., The Diphasic Erosive Action of Salts on the Cholate Gel," by S. B. Schryver and Mary Hewlett. "Some Photochemical Experiments with Pure Chlorophyll and their bearing on Theories of Carbon Assimilation," by I. Jorgensen and F. Kidd.

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THE CHEMICAL NEWS

Vol. CXIV., No. 2972.

ON THE CORRECT ADJUSTMENT OF CHEMICAL WEIGHTS.[*]

By WILLIAM CROOKES, F.R.S.

A SET of grain or gramme weights, as ordinarily supplied by even the best instrument-maker, is never absolutely exact. However carefully they may be adjusted, the pieces of metal which respectively represent 1000 grains, 100 grains, 10 grains, &c., are only more or less approximations to the true weights. It is impossible for any one to adjust them with absolute accuracy. Indeed, the best makers readily acknowledge this, and are careful not to guarantee the correctness of their weights beyond certain limits.

In most chemical analyses the error arising from inaccuracies in the weights used is so small in comparison to errors of manipulation, or to imperfections inherent in the chemical processes adopted, that it may generally be disregarded; but when the chemist has for his object the determination of an atomic weight, or is engaged in other researches demanding the highest refinement of accuracy which chemistry and physics can supply, then he is bound to neglect no correction which will increase the precision of the results.

That chemists, whose well-trained reasoning powers allow them to take for granted nothing which is capable of experimental verification, and who insist upon the utmost attainable precision in their balances, should, as a rule, entirely neglect the probable errors which the inaccuracies of their weights may introduce, is somewhat surprising.

For the four last years I have been engaged in an investigation, the results of which will shortly appear in this journal. In carrying out this investigation, it has been my endeavour to avail myself of every possible refinement to ensure accuracy. In order to eliminate the errors introduced by varying atmospheric pressure, the weighings, and many of the chemical reactions have been performed in a vacuum. It is not my intention in the present paper to discuss the subject of weighing *in vacuo*: but as many friends from time to time, whilst witnessing my methods of weighing, have expressed a wish to have placed on record, for future reference, the plan adopted for adjusting weights, and as, moreover, I am not cognisant of the existence of any published directions, except those cited below, I am induced to place a short notice of my method of procedure before the readers of the CHEMICAL NEWS. Let me commence by disclaiming any originality in the process. Professor W. H. Miller, of Cambridge, in his classical researches on the determination of the standard pound (*Philosophical Transactions* for 1856, pp. 811, 827, 937), has given full directions for attaining a similar object. These, however, will not exactly apply to the systems of weights used by chemists; for of the three cases described by him, the former two concern a peculiar system of weights, and in the third, two sets of weights, one for the Exchequer, the other for the Royal Mint, were compared at the same time. To this paper, as well as to the learned author himself, I am indebted for an immense store of valuable information on the subject of weights and weighings.

It may make this description clearer if I give exactly as they were performed the details of the adjustment of a set of brass grain-weights, with which some of my earlie researches were carried out. These weights, new, and made by one of the best English firms, Messrs. Ladd and Oertling, may, therefore, be considered as accurate a set as any in ordinary use.

For nearly every process in which weights are used in chemistry, the object is not to ascertain the *absolute* weight of a substance in terms of a grain or gramme, but to determine its *relative* weight, in comparison with that which it possessed at some other time before it was submitted to certain analytical or synthetical operations. If the weighings are performed with the same weights, it does not at all matter whether the weights are absolutely of the value which they profess to be, but it is very important that they should bear a known proportion to each other. The highest weight (1000 grains) in the set should be taken as the standard. It is immaterial whether or not this is accurately 1000 standard grains,[*] but, *calling it* 1000 grains, the value of the other weights should be known in terms of this weight with the greatest attainable accuracy.

The first operation consists in taking the specific gravities of each brass weight. The density of the larger weights must be ascertained at least to the second place of decimals, and that of the smaller ones to the first place. The specific gravity of each weight should be separately determined; for brass weights, even of the same set, differ greatly in density among themselves. A variation of not more than 0·05 in the specific gravity of the 1000 grain weight, will cause a difference in the amount of air it displaces of about 0·001 grain.

The balance being brought into equilibrium, the 1000 grain weight is placed in the left pan, and in the right are placed the 600, the 300, and the 100 grain weights. It is now found that, to bring the balance back to equilibrium, a slight additional weight has to be placed on the right side, to supplement the three weights already in that pan. This is noted. The weights are then removed to the opposite pans, the 1000 grains being on the right, and the three smaller weights on the left. It is now found that a small weight has to be subtracted from the side carrying the three weights, in order to produce equilibrium. The weights are removed and interchanged in this manner ten times, so as to eliminate, as far as possible, the errors arising from observation, or the unequal expansion by heat of the arms of the balance; and by applying the method of least squares to the results obtained, we at last arrive at the equation—

$$(1000)^{\dagger} = (600) + (300) + (100) + 0{\cdot}00106 \text{ grains} \quad . \quad . \quad a$$

In a similar manner the values of the (600), the (300), and the (100) weights are ascertained in terms of the other weights, thus—

$$(600) = (300) + (200) + (100) - 0{\cdot}00485 \text{ grains} \quad . \quad b$$
$$(300) = (200) + (100) - 0{\cdot}00574 \text{ grains} \quad . \quad . \quad . \quad c$$
$$(200) = (100) + (60\ ) + (30) + (10) + 0{\cdot}00057 \text{ grains} \ . \quad d$$
$$(100) = (60\ ) + (30\ ) + (10) + 0{\cdot}00105 \text{ grains} \ . \quad . \quad e$$

We now have data for ascertaining the absolute values of the larger weights in terms of the (1000) weight, taken as standard. Adding *a* and *b* together gives—

$$(1000) = 2\,(300) + (200) + 2(100) + 0{\cdot}00591 \text{ grains} \ . \quad f$$

Multiplying *c* by 2 gives—

$$2(300) = 2(200) + 2(100) - 0{\cdot}01148 \text{ grains} \quad . \quad . \quad g$$

Subtracting *e* from *d* gives—

$$(200) = 2(100) - 0{\cdot}00048 \text{ grains} \quad . \quad . \quad . \quad . \quad h$$

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[*] Reprinted from the CHEMICAL NEWS, vol. xv., No. 385, April 19, 1867, at the request of many readers.

[*] This must be understood as referring only to ordinary chemical research in synthesis or analysis. In many physical investigations it is of great importance that the 1000 grain weight should really represent 1000 normal grains, or that its deviation from that value should be accurately determined. But I confess I do not know where a standard weight suitable for such a comparison is to be met with.

[†] For distinctness, when speaking of the pieces of brass which are stamped 1000, 600, 100 grains, &c., I represent them by their nominal value enclosed within brackets.

Now, by adding *f*, *g*, and three times *h*, we get—

$$(1000) = 10(100) - 0{\cdot}00701$$

$$\therefore \frac{(1000)}{10} = (100) - 0{\cdot}000701$$

and

$$\therefore (100) = 100{\cdot}000701 \text{ grains.}$$

Substituting this value for the (100) weight, we get from equation *e*—

$$100{\cdot}000701 \text{ grains} = (60) + (30) + (10) + 0{\cdot}00105 \text{ grains,}$$

or

$$(60) + (30) + (10) = 99{\cdot}999651 \text{ grains.}$$

From equation *d* we get—

$$(200) = 100{\cdot}000701 + 99{\cdot}999651 + 0{\cdot}00057 \text{ grains,}$$

or

$$(200) = 200{\cdot}000922 \text{ grains.}$$

From equation *c* we get—

$$(300) = 200{\cdot}000922 + 100{\cdot}000701 - 0{\cdot}00574 \text{ grains,}$$

or

$$(300) = 299{\cdot}995882 \text{ grains.}$$

From equation *b* we get—

$$(600) = 299{\cdot}995882 + 200{\cdot}000922 + 100{\cdot}000701 + \\ + 0{\cdot}00485 \text{ grains,}$$

or

$$(600) = 600{\cdot}002355 \text{ grains.}$$

The next step is to ascertain the value of the smaller weights. It is now necessary to obtain a second 10 grain weight. This I will call (x); and I will assume that—

$$(60) + (30) + (10) = 100 \text{ grains} \pm i.$$

(In this case, from equation *e*, the value of i is seen to be—0·00035 grain).

By an exactly similar mode of intercomparison, the following equations are now obtained:—

$$(60) = (30) + (20) + (10) + 0{\cdot}00270 \quad . \quad . \quad . \quad . \quad k$$
$$(30) = (20) + (10) - 0{\cdot}00037 \quad . \quad . \quad . \quad . \quad . \quad l$$
$$(20) = (10) + (x) - 0{\cdot}00103 \quad . \quad . \quad . \quad . \quad . \quad m$$
$$(10) = (x) \pm 0{\cdot}00000 \quad . \quad . \quad . \quad . \quad . \quad . \quad n$$

Then, by repeating the above process of adding, multiplying, or subtracting, we finally get the true values of these smaller weights. The same process is then to be extended to the whole of the other weights.

The value of the weights thus given is, however, their weight in *air* of the ordinary pressure. It therefore becomes necessary to reduce them to what they would be worth in a vacuum. All bodies displace a bulk of air equal to their own volume, and the weight of this air is therefore greater as their specific gravity diminishes. In delicate investigations this loss of weight in air is important; for 7000 grains of brass displace, roughly, one grain of air.

By proceeding according to known rules, the value of the weights *in vacuo* is finally ascertained, and the results are embodied in the following table.* It is assumed that the (1000) weight really weighs 1000 grains in air:—

Names of the weights.	Value in air in terms of the (1000) grain weight.	Value *in vacuo* in terms of the (1000) grain weight.	Weight of air displaced by each.	Volume of weights in grs. of water of maximum density.
	grains.	grains.	grains.	
(1000) .	1000·0000	1000·1462	0·1462	119·193
(600) .	600·0023	600·0904	0·0881	71·812
(300) .	299·9959	300·0401	0·0442	36·035
(200) .	200·0009	200·0303	0·0294	23·930
(100) .	100·0007	100·0153	0·0146	11·868
(60) .	60·0007	60·0091	0·0084	7·140
(30) .	29·9988	30·0040	0·0052	3·538
(20) .	19·9991	20·0030	0·0039	2·358
(10) .	10·0001	10·0015	0·0014	1·166

Because these corrections are individually small, it is not right to assume that they may be neglected. The weights submitted to the above adjustment were exceptionally good, and must not be considered as fair representatives of those usually employed in analysis. I have met with weights in which the deviations from their true values were one hundred times as great as in the foregoing instance; and as no one can be certain that some of his weights are not faulty, it is best to ascertain their relative values once for all; for as the deviations are sometimes in excess and sometimes in defect, they are liable to accumulate in one or the other direction, and thus produce errors in weighing of considerable magnitude.

Having ascertained their true value, the weights ought to be carefully preserved. No attempt should be made to get them more accurately adjusted by adding to or removing portions of the metal, and they should not be picked up with metal forceps, as they suffer thus by wear and become lighter.

When possible the chemist should always use platinum weights. After adjusting the weights in question, I found that, owing to the accumulation of tarnish on their surface, there was danger of their becoming faulty. I accordingly procured from Messrs. Johnson and Matthey another set, the separate weights of which were turned out of bars of well-fused platinum. After having bestowed several months' labour upon them, I have now the satisfaction of knowing that they are as near perfection as could reasonably be expected. They have been in use for nearly three years, both in air of the ordinary pressure and *in vacuo*, and comparisons made a few days ago show that their values remain absolutely unaltered.

THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

(Sixth Communication).*

By LEROY McMASTER and A. C. MAGILL.

(Continued from p. 221).

Ammonium α-Bromopalmitate.—We could find no record of the preparation of this salt. When prepared by passing ammonia into an ether solution of the acid it precipitated first as a gelatinous mass, which soon changed to an amorphous powder. It could not be precipitated in alcohol, owing to its solubility in that solvent, but when a saturated alcoholic solution of the acid, into which ammonia had been passed for some time, was poured into a rather large volume of ether the salt formed in fine frost-like crystals.

The salt dissolves easily in water. The solution lathers copiously on shaking. We have here another example of an ammonium soap. This is true of the ammonium salts of all the higher fatty acids, such as capric acid, caprylic acid, myristic acid, &c. The neutral aqueous solution hydrolyses very slowly. The salt is very soluble in acetic acid, methyl alcohol, and ethyl alcohol. When the ethyl alcohol solution of the salt is warmed there is some decomposition of the salt and an ester is formed. The salt is insoluble in ether, benzene, and chloroform, and slightly soluble in acetone. It loses ammonia very slowly in dry air and rapidly in moist air. It gives off but little ammonia at 50°, but decomposition takes place rapidly at 100°. The salt is not hygroscopic.

Calc. for $C_{15}H_{30}BrCO_2(NH_4)$:—3·99 per cent N.
Found:—3·95 per cent (ether); 3·95 per cent (ether-alcohol mixture).

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* To avoid extending the table to unnecessary limits, I omit the weights below 10 grains

* For previous papers on this subject see Chem. News, 1913, cviii., 136; 1913, cviii., 182, 193; 1914, cx., 212; 1914, cx., 224; 1915, cxii., 187. From the *Journal of the American Chemical Society* xxxviii., No. 9.

Ammonium palmitate, described in a previous paper by McMaster (*loc. cit*).), and ammonium bromopalmitate can both be prepared in ether. The first is soluble in acetone while the second is only slightly soluble. Both are soluble in water, methyl alcohol, and ethyl alcohol. Both lather very freely in water, indicating ammonium soaps. The aqueous solution of the palmitate hydrolyses much more rapidly than that of the bromopalmitate. The latter decomposes in the air more slowly than the first. Neither salt is hygroscopic.

Ammonium α-Bromostearate.—As in the case of the corresponding bromopalmitate no record of this salt can be found in the literature. It was prepared in ether as a non-crystalline compound. It was also precipitated from an alcoholic ammonia solution of the acid upon the addition of ether. In this case it formed small white crystals. The aqueous solution lathers freely on shaking and very slowly becomes acid. The salt is not deliquescent. It is stable in dry air but loses ammonia in moist air. It is soluble in methyl and ethyl alcohols, slightly soluble in cold acetone and readily soluble in hot acetone. It does not dissolve in ether, ethyl acetate, benzene, or chloroform. When treated with acetic acid α-bromostearic acid is formed. The salt decomposes slowly with the liberation of ammonia both at 50° and 100°.

Calc. for $C_{17}H_{34}BrCO_2(NH_4)$: —3·69 per cent. Found:—3·66 per cent N.

The neutral ammonium salt of α-bromostearic acid can thus be prepared in ether as well as the neutral salt of stearic acid. The preparation and properties of this latter salt have been previously described by McMaster. Both salts are soluble in water, methyl alcohol, ethyl alcohol, and acetone. In the last solvent the bromostearate is less soluble than the stearate. Both salts are not hygroscopic, do not lose ammonia in dry air, but do in moist air.

Comparison of Results.—Including those neutral-ammonium salts described in the previous papers there have thus far been prepared and studied twenty-two salts of the saturated monobasic acids of the aliphatic series, or derivatives of acids of that series. We have found that there is a very wide variation in many of their properties. There seems to be no uniformity in their action when exposed to the air. Some of them do not deliquesce, some do so very slowly, and some very rapidly. Some of these salts lose ammonia in the air with varying degrees of rapidity, while others of them do not lose ammonia. Most of these salts hydrolyse, but not all of them. They all have the general property of being soluble in water and more or less so in the alcohols. Most of them are slightly soluble in acetone. All are insoluble in benzene and ether. A few of them have also been found to be insoluble in ethyl acetate.

Some Monobasic Unsaturated Acids.

Ammonium Acrylate.—When dry ammonia was passed into an ether solution of acrylic acid a gelatinous mass was formed. This condition did not change when the substance was dried in an atmosphere of ammonia. This same gelatinous, glue-like mass was formed also in an alcoholic solution of the acid, even when the solution was packed in ice. We also attempted to prepare the salt in acetone. On passing in the ammonia there was formed at first a white precipitate, which very soon redissolved and formed a light brown solution. The heat of reaction was sufficient to raise the temperature almost to the boiling-point of the acetone. No doubt there was formed here again some diacetoamine, in which the salt which first formed was redissolved. The results in this case were the same as we had in the case of the glycolic acid.

The neutral ammonium acrylate was finally prepared by passing the ammonia into a benzene solution of the acid and evaporating off the benzene. Monoclinic crystals were obtained. If a solution of the acid in ethyl acetate be used the acid separates as a fine granular mass. The salt prepared in either medium is not hygroscopic, does not lose ammonia when exposed to dry or moist air, and does not decompose when warmed to 100°. After standing several months the salt developed the odour of acrylic acid. An aqueous solution of the salt slowly hydrolyses.

The salt is soluble in water and acetic acid, slightly soluble in methyl and ethyl alcohols, and insoluble in ether, chloroform, ethyl acetate, acetone, and benzene. No previous record of this salt could be found.

Calc. for $CH_2CHCO_2(NH_4)$: — 15·73 per cent. Found:—15·69 per cent N (benzene). Prepared in ethyl acetate. Found:—15·70 per cent. N.

Ammonium β-Chlorocrotonate.—Sarnow (*Ann.*, 1872, clxiv., 99) prepared the ammonium salt of the α-acid by treating the acid with a saturated solution of ammonium carbonate. He found that the salt crystallised out from the solution in plate-like crystals, which sublimed at 100°. No mention is made of the ammonium salt of the β-acid.

When prepared by our method the salt of the β-acid was precipitated from an ether solution as small flaky crystals. The salt is very soluble in ethyl alcohol, but can be prepared by pouring a saturated alcoholic ammonia solution of the acid into ether. It here separates out as a fine white crystalline mass. The salt was also precipitated as fine crystals in acetone.

The salt is not hygroscopic. It is very soluble in water and forms a neutral solution, which soon hydrolyses. The salt is stable in dry air but loses ammonia slowly in moist air. The salt is also very soluble in methyl alcohol and acetic acid as well as in ethyl alcohol. It is only slightly soluble in acetone and ethyl acetate. It is insoluble in ether, chloroform, and benzene. It can be dried at 100° without decomposition.

Calc. for $C_3H_4ClCO_2(NH_4)$:—10·18 per cent N. Found:—10·14 per cent (ether); 10·19 per cent (acetone); 10·15 per cent (ether-alcohol mixture).

Ammonium crotonate has been described by McMaster. It was prepared, as we have prepared the β-chlorocrotonate, in ether and in a saturated alcoholic solution of the acid. In the case of the β chlorocrotonate it was necessary to add ether to the alcoholic ammonia solution before precipitation took place. Both salts separate from ethyl alcohol in a crystalline condition, and both are readily soluble in water. The aqueous solution in each case quickly hydrolyses. Both salts are also soluble in methyl alcohol and acetic acid and insoluble in chloroform and ether. Neither salt is deliquescent.

Ammonium Erucate.—A cream-coloured, amorphous precipitate of this salt formed when ammonia was passed into the ether solution of the acid. Erucic acid is only slightly soluble in ethyl alcohol, and we thus obtained a small yield of white crystals in this solvent. The solution of the salt in water also lathers freely on shaking. The aqueous solution, neutral at first, hydrolyses. The salt does not lose ammonia in dry air, but does so very slowly in moist air. It is not hygroscopic and can be dried at 100° without decomposition.

The salt is very slightly soluble in ethyl alcohol and somewhat more soluble in methyl alcohol. It crystallises from the latter in monoclinic crystals. The salt is sparingly soluble in acetone and insoluble in ether, ethyl acetate, and benzene. It is readily soluble in acetic acid.

Calc. for $C_{21}H_{41}CO_2(NH_4)$: — 3·94 per cent N. Found:—3·91 per cent (ether); 3·95 per cent (ethyl alcohol).

The literature makes no mention of this salt, so far as we can find.

Comparison of Results.—The neutral ammonium salts of crotonic, oleic, and elaidic acids have been described by McMaster in previous papers. With the exception of ammonium acrylate the salts of the unsaturated monobasic acids can be prepared in ether, from which they separate in gelatinous masses, which gradually change over to amorphous solids. Ammonium oleate can be prepared in a crystalline form if ammonia is passed in for a sufficient length of time. The acrylate can be prepared in ethyl acetate. These salts are all soluble in ethyl alcohol, methyl alcohol, and water. They all separate from an alcoholic solution on evaporation as fine white crystals. Their aqueous solutions hydrolyse. They are not deliquescent.

The Substituted Malonic Acids.

Ammonium Dimethylmalonate.—There is no mention in the literature of the neutral ammonium salts of the substituted malonic acids included in this investigation. Ammonium dimethylmalonate can be prepared from a solution of the acid in ether or ethyl alcohol by our method. In ether it is precipitated as a curdy mass, which on washing and drying becomes a white amorphous powder. In alcohol it is precipitated as crystals.

The salt forms a neutral solution in water and soon hydrolyses. The salt is very deliquescent and gives off ammonia slowly in dry air and very rapidly in moist air. It decomposes into ammonia and the acid when heated to 50°. The salt is readily soluble in methyl alcohol and acetic acid, slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, benzene, chloroform, and acetone.

The neutral salt can also be prepared in ethyl acetate and acetone. From each of these solvents it readily precipitates in a crystalline form.

> Calc. for $(CH_3)_2C(CO_2NH_4)_2$:—16·87 per cent N. Found:—16·80 per cent (ether); 16·79 per cent ethyl alcohol; 16·81 per cent (ethyl acetate); 16·85 per cent (acetone).

Ammonium Dipropylmalonate.—This salt was prepared from solutions of the acid in ether, ethyl alcohol, ethyl acetate, and acetone. From ether it was precipitated as a gelatinous mass which changed to hard lumps. These lumps were crushed, washed, and dried. From solutions of the acid in ethyl alcohol, ethyl acetate, and acetone the neutral salt precipitated as white monoclinic crystals. It was necessary to surround the ethyl alcohol solution with ice to prevent the formation of an ester. The salt formed a solution in water which remained neutral for at least several days. It is slightly deliquescent. It does not give off ammonia in dry or moist air. There is no decomposition at 50°, but at 100° ammonia is slowly evolved.

The salt is readily soluble in acetic acid and methyl alcohol. It is slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, acetone, chloroform, and benzene.

> Calc. for $(C_3H_7)_2C(CO_2NH_4)_2$:—12·61 per cent N. Found:—12·59 per cent (ether); 12·58 per cent (ethyl alcohol); 12·56 per cent (ethyl acetate); 12·62 per cent (acetone).

Ammonium Isopropylmalonate.—On addition of dry ammonia to an ether solution of the acid this salt formed as a mucilaginous precipitate, which on drying collected in hard lumps. From ethyl alcohol it precipitated as white crystals.

The salt is very deliquescent, and on exposure to moist air breaks up into ammonia and the acid. It is stable in dry air at ordinary temperatures. At 50° it gives off ammonia slowly. At 100° the decomposition is somewhat more rapid.

An aqueous solution of the salt remains neutral to litmus. The salt is very soluble in methyl alcohol and acetic acid. It is very slightly soluble in ethyl alcohol and benzene and insoluble in acetone, ethyl acetate, and chloroform.

> Calc. for $C_3H_7CH(CO_2NH_4)_2$:—15·55 per cent N. Found:—15·52 per cent (ether); 15·50 per cent (ethyl alcohol).

Ammonium Butylmalonate.—From a solution of the acid in ether this salt precipitated in asbestos-like fibres, which dried to a hard mass. From ethyl alcohol it precipitated as rhombic crystals. In order to prevent the formation of some ester it was necessary to keep the alcohol solution packed in ice.

The salt is slightly deliquescent, and readily dissolves in water to form a neutral solution, which soon becomes acid to sensitive litmus. The salt is stable in dry air at room temperature, but at 50° ammonia is slowly evolved. It loses ammonia rapidly in moist air or when heated to 100°. The salt is very soluble in methyl alcohol and acetic acid, slightly soluble in ethyl acetate, and insoluble in ethyl alcohol, ether, acetone, chloroform, and benzene.

> Calc. for $C_4H_9CH(CO_2NH_4)_2$:—14·45 per cent N. Found:—14·40 per cent (ether); 14·40 per cent (ethyl alcohol).

Ammonium Allylmalonate.—Dry ammonia precipitated this salt as a fibrous mass from an ether solution of the acid. On drying this precipitate it formed as hard lumps. It formed as a white crystalline compound of an ethyl alcohol solution of the acid. The heat of neutralisation in the ethyl alcohol was sufficient to form some ester unless the solution was packed in ice. The salt was also prepared in acetone. The crystals resembled those formed in the alcohol.

The salt is very deliquescent and loses ammonia rapidly in both dry and moist air. It is difficult to prevent decomposition of the salt even during the drying of it. It decomposes very rapidly at 50° and before 100° is reached the salt loses all its ammonia.

The aqueous solution of the salt, which is at first neutral, hydrolyses on standing. The salt is readily soluble in methyl alcohol and acetic acid, very slightly soluble in ethyl alcohol, ethyl acetate, and acetone, and insoluble in chloroform, ether, and benzene.

> Calc. for $C_3H_5CH(CO_2NH_4)_2$:—15·73 per cent N. Found:—15·74 per cent (ether); 15·70 per cent (ethyl alcohol); 15·70 per cent (acetone).

Ammonium Benzylmalonate.—This salt readily precipitated in a non-crystalline condition from a solution of the acid in ether. It precipitated as hexagonal crystals from a solution of the acid in ethyl alcohol. Neither the crystalline nor the non-crystalline form was hygroscopic.

The salt does not lose ammonia in dry or moist air even at 50°, but an analysis of a sample kept at 100° for ten minutes showed that some decomposition had taken place. The salt dissolved readily in water, to which it imparted a neutral reaction. This solution remained neutral at least twenty-four hours. The salt is also very soluble in acetic acid and methyl alcohol, but only sparingly so in ethyl alcohol, ethyl acetate, and chloroform. It is insoluble in ether, acetone, and benzene.

> Calc. for $C_6H_5CH(CO_2NH_4)_2$:—13·08 per cent N. Found:—13·05 per cent (ether); 13·04 per cent (ethyl alcohol).

Comparison of Results.—Previous papers by one of us (McMaster, *loc. cit.*) have given an account of the preparation and properties of the neutral ammonium salts of malonic acid and ethyl malonic acid. We have just described the neutral ammonium salts of six other substituted derivatives of malonic acid. All of these salts precipitate in ether as amorphous compounds and as fine white crystals in ethyl alcohol. They are all very soluble in water and insoluble in ether and benzene. With the exception of the allyl compound all are insoluble in acetone. Most of them lose ammonia in moist air. The aqueous solutions of the salts of dimethyl, butyl, and allylmalonic acids hydrolyse. The aqueous solutions of the others do not hydrolyse. The salts of malonic and benzylmalonic acids do not deliquesce, while all the others do. The most striking characteristics common to all these malonates is their solubility in the common alcohols. All of them are soluble in methyl alcohol, and, with the exception of the butylmalonate, all are only very slightly soluble in ethyl alchol. The butylmalonate is insoluble in this solvent.

(To be continued).

THE

UTILISATION OF AROMATIC HYDROCARBONS DERIVED FROM CRACKED PETROLEUM.*

By W. F. RITTMAN.

In the course of the commercial development of the vapour-phase cracking process for the production of benzene and toluene from petroleum, numerous chemical problems have arisen. One of the most important is the utilisation of the products obtained, since these necessarily differ from those derived from coal. The idea is widely prevalent that petroleum-derived products are inferior, and a principal object of the present work has been to show that this prejudice is due entirely to a lack of knowledge concerning proper methods of utilisation.

The immediate cause for the present work has been the necessity of demonstrating that petroleum-derived toluene can be successfully converted into trinitrotoluene in a commercially practicable manner.

Differences between Coal-derived and Petroleum-derived Hydrocarbon Mixtures.

A brief consideration of the sources and methods of production of the two types of commercial hydrocarbon mixtures serve to indicate the nature of the present problem.

The coal-derived products are the results of decomposition of the original material at high temperatures, which fact influences to a large degree the composition of these mixtures. The aromatics are associated with varying quantities of such impurities as sulphur, oxygen, and nitrogen bodies, as well as non-aromatic hydrocarbons of various degrees of unsaturation. Condensable paraffins are not, however, stable at the temperatures which occur during the destructive distillation of coal, and these hydrocarbons are therefore absent from products derived from this source. It follows therefore that aromatic products obtained from coal contain objectionable impurities from which, however, they may be freed if subjected to treatment by proper physical and chemical processes. On the other hand, the cracking of petroleum yields aromatics which are entirely free from oxygen containing impurities, and which at worst carry only minute quantities of sulphur and nitrogen bodies. The chief and practically the only impurities are olefins and paraffins. These paraffins are necessarily present because maximum yields of toluene and benzene cannot be obtained under conditions which entirely break down these saturated compounds, and, furthermore, it is difficult or even impossible to get rid of them completely. Methods of fractional distillation do not effect complete separation, and chemical methods are ineffective, since the aromatics are more reactive than the paraffins.

Thus, in attacking the present problem it has been granted that it may be difficult or even impossible to obtain pure aromatics from cracked petroleum. Experiments have therefore aimed at devising methods of utilisation suitable for the impure products, and it now appears that these methods have commercial advantages over those in use for coal-derived products, although the latter substances cannot be treated in the same way as the petroleum products, since the sulphur, oxygen, and nitrogen bodies are not chemically inactive, as are the paraffin hydrocarbons.

Methods of Preparation and Properties of the Nitrotoluenes.

Trinitrotoluene is obtained from toluene by a process of nitration occurring in three successive stages and involving the intermediate formation of mononitrotoluene and dinitrotoluene.

$$1.\quad \underset{\text{Toluene.}}{C_7H_8} + HNO_3 \rightleftarrows \underset{\text{Mononitrotulene.}}{C_7H_7(NO_2)} + H_2O$$

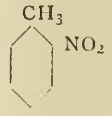
$$2.\quad \underset{\text{Mononitroluene.}}{C_7H_7(NO_2)} + HNO_3 \rightleftarrows \underset{\text{Dinitrotoluene}}{C_7H_6(NO_2)_2} + H_2O$$

$$3.\quad \underset{\text{Dinitrotoluene.}}{C_7H_6(NO_2)_2} + HNO_3 \rightleftarrows \underset{\text{Trnitrotoluene.}}{C_7H_5(NO_2)_3} + H_2O$$

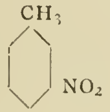
The extent to which the nitration may proceed to any one of the above stages is controlled by conditions of treatment, and particularly by the factor of acid concentration. This can be regulated by adjustment of the quantity of nitric acid employed, and also by varying the amount of sulphuric acid mixed with the nitric to take up and render inactive the water which is one of the reaction products.

Properties of the Nitrotoluenes.

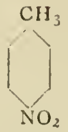
Mononitrotoluene, $C_7H_7NO_2$, exists in three isomeric forms, ortho-, meta-, and ara .—



o-Nitrotoluene.



m-Nitrotoluene.



p-Nitrotoluene.

The physical properties of these compounds are indicated below :—

Mononitrotoluene.	Melting-point.	Boiling-point.	Specific gravity
Ortho ..	– 10·5°	218°	1·168(15°/15°)
Meta ..	16·0°	231°	1·168(15°/15°)
Para ..	54·0°	238°	1·231(54°/4°)

Direct nitration of toluene yields a mixture of the three isomers, which, however, contains little of the meta product. This is in accord with the law of substitution in the benzene ring, the methyl group being one which controls the ortho- and para-positions.

Dinitrotoluene exists in six possible isomeric forms, all solids. These are designated by numbers, the position occupied by the methyl group being No. 1.

Dinitrotoluene.	2 : 4.	3 : 4.	2 : 3.	2 : 6	3 : 5.	2 :
Melting-point (°)	70·5	60·0	63·0	61·0	93·0	52·5

The dinitrotoluene produced by the nitration of toluene or of the commercial mixture of *o*- and *p*-nitrotoluenes consists chiefly of the 2 : 4 and 2 : 6 products.

Trinitrotoluene is theoretically capable of existing in six isomeric forms. Of these the 2 : 4 : 6, the 2 : 3 : 4, and 2 : 4 : 5 compounds have been prepared. The 2 : 4 : 6, or "symmetrical" compound, is the best known, and is by far the chief constituent of the commercial product.

Trinitrotoluene.	2 : 4 : 6.	2 : 3 : 4.	2 : 4 : 5.
Melting-point (°).. ..	80·6	112·0	104·0

Pure nitrotoluene is a white solid of absolutely neutra reaction and of unusual stability. The commercial product is generally pale yellow. Trinitrotoluene is very slightly soluble in water, either hot or cold. It is sparingly soluble in cold alcohol, but readily in hot, this solvent being one commonly used for the process of recrystallisation.

Trinitrotoluene is by far the most valuable explosive now used in military service for bursting charges. The substance may be manufactured with comparative safety and is free from danger of deterioration. It is non-acid and does not act upon metals with which it may come in contact. The lowness of its melting-point makes easy the filling of shells and containers, which is accomplished by the simple process of pouring the molten explosive. Trinitrotoluene is sufficiently inert so that the possibility of accidental explosion through concussion is practically nil. It is stated that a shell filled with it may be made to penetrate steel plates without setting off the explosive through the shock. Detonation is accomplished after penetration by means of a time fuse.

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* Published with the permission of the Director of the Bureau of Mines. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 12.

Commercial Preparation of Trinitrotoluene.

The commercial preparation of trinitrotoluene is accomplished in either of two general ways:—(1) The process may be completed in one stage, or (2) it may be accomplished in several successive stages. In any event, it has been found commercially undesirable, in this country at least, to purify the final product by any process of crystallisation or washing which involves the use of organic solvents. The purity of trinitrotoluene is generally determined by its melting-point, and present specifications place this at 75° C., which is about 5° below the melting-point of the pure compound. It has been found possible to attain the desired degree of purity by a simple process of water washing, providing conditions of preparation are right.

The Single Stage Process of nitration is, of course, simple in operation and requires a minimum of plant equipment. It has the decided disadvantage, however, of being uneconomical in acid consumption. The process requires a considerable concentration of acid at the end of the reaction, and the resulting spent acid cannot be utilised in the single stage method, although its strength is considerably greater than would be necessary in the earlier stages of the other general process.

Processes involving Several Stages, with complete or partial purification of intermediate products are, of course, expensive as regards cost of labour and plant equipment. They do, however, permit economic utilisation of acid, since the spent acid from the final stage may be employed in an earlier stage of the next cycle, obviating the necessity of discarding any but a thoroughly exhausted waste acid. In addition, as has been shown by the results of the present experiments, the polystage process permits the use of a less expensively purified raw material.

The preparation of trinitrotoluene involves the removal of water-insoluble impurities from the final product, or from some one of the other substances, dinitrotoluene, mononitrotoluene, or toluene. Processes involving the use of coal-derived toluene have been dependent upon the purification of the initial substance. In the past, when specifications were more exacting, and especially abroad, crystallisation of the final product has been resorted to, but this is not practicable under present conditions. The purification of dinitrotoluene involves the same methods as need be applied to trinitrotoluene, and that possible medium for purification is likewise eliminated.

Scope aad Plan of present Work.

The present work has been based upon the device of purifying the mono-substitution product. The whole proposition may be stated concisely as follows:—

The preparation of satisfactory trinitrotoluene involves a purification from water-insoluble impurities of one of the four substances, toluene, mononitrotoluene, dinitrotoluene, or trinitrotoluene. Both toluene and mononitrotoluene are liquids having boiling-points sufficiently low that their distillation is a matter involving no inherent difficulty. The purification of dinitrotoluene and trinitrotoluene can be accomplished only through commercially impracticable processes of crystallisation or washing which involve the use of organic solvents.

Toluene derived from petroleum cannot be brought to a state of complete purity readily by any methods now known, but by means of simple processes of fractionation it is possible to obtain, from cracked petroleum, toluene with no impurities save paraffin and olefin bodies. The olefins may be removed by extraction with sulphuric acid, and the resulting mixture, when nitrated under proper conditions of acid concentration, yields mononitrotoluene contaminated with the original paraffins, with resinous bodies formed by the action of the acid, and possibly with a small quantity of dinitrotoluene.

Mononitrotoluene boils between 218° C. and 238° C., the paraffins in the neighbourhood of 110°, and the resins, &c., at temperatures above 300° C. Hence, a simple distillation, preferably *in vacuo* or with steam, gives an easy and practically complete separation of mononitrotoluene from the low boiling paraffins and the higher boiling resins.

Since no water-insoluble impurities are present in the mononitrotoluene it may be converted readily into trinitrotoluene by commercially practicable methods.

Experimental.

Samples of toluene were obtained which had been prepared by simple distillation, and redistillation of cracked petroleum from the commercial furnaces employed in the Bureau of Mines vapour-phase cracking process.

Mononitrotoluene.—The first section of the work involved the preparation of pure mononitrotoluene, and this process was studied in detail. Large quantities were not used, but data were obtained which can be applied with some exactness to commercial work. It was shown conclusively that no difficulties need be encountered in large scale operations. The mononitrotoluene prepared was analysed carefully for its purity, as indicated by nitrogen content. Yields were also measured, although no emphasis is laid on these since the scale of operation made them necessarily low.

Trinitrotoluene.—The analyses of the mono product indicated that it was almost chemically pure, but it was thought desirable to actually convert it into the higher substituted compound. Samples of trinitrotoluene were therefore prepared; these, when washed with water, showed melting-points of 75° and above. In the course of these preparations valuable indications were obtained as to advantageous methods of procedure for large scale operations, although no final details were worked out.

Nitrobenzene.—Finally a simple experiment was performed to verify the obvious conclusion that benzene mixtures would behave in a manner indentical with those containing toluene. Nitrobenzene was prepared by the method used for mononitrotoluene. The resulting product was tested by conversion into aniline by the method outlined by Gattermann ("Practical Methods of Organic Chemistry," second English from fourth German edition, 1907, p. 188). This section of the work was purely qualitative, and no figures were obtained, but it may be stated that the preparations involved no difficulty, and that the behaviour of the benzene product was identical with that of the toluene.

Original Materials.—The original materials were toluene fractions obtained from petroleum cracked by the Bureau of Mines vapour-phase process. The oils were distilled in commercial Badger stills. Analyses of the products yielded the following figures:—

	Sample No. 1.	Sample No. 2.
Distillation range	109°—115°	
Specific gravity, 15°/15° ..	0·832	0·823
Toluene content, on basis of sp. gr. (*a*)	72·9 per cent	66·4 per cent

(*a*) Rittman, Twomey, and Egloff, *Met. Chem. Eng.*, 1915, xiii., 682.

Preparation of Mononitrotoluene.—The method employed for the preparation of mononitrotoluene was that of Schultz and Flachslander (*Journ. Prakt. Chem.*, 1902, [2], lxvi., 156):—

The nitration is conducted in a wide-mouthed round-bottomed flask fitted with a thermometer (bulb immersed

Table I.—*Mononitrotoluene from Toluene* (100 *Grms. Sample—Toluene Content as given*).
(The preliminary treatments for removal of olefins are described in the text).

Type of nitration	Exp. No.	Mixed acid. Grms.	Toluene used. Grms.	Yield of crude mononitrotoluene. Grms.	Yield of purified (distilled) mononitrotoluene.					
					Grms. yield.		Per cent nitrogen (*a*).		Actual per cent.	
					Actual.	Theoretical.	Actual.	Theoretical	Yield.	Purity.
Olefins present..	1	253	72·9	95·0	79·0	108·5	10·16	10·21	72·7	99·5
Olefins removed, sample washed and redistilled	2	253	97·0	127·0	104·5	144·5	10·19	10·21	73·2	99·8
Olefins removed, no washing or redistillation ..	3*a*	253	88·5	127·0	36·4	131·8	10·19	10·21	66·6	99·8
	3*b*	253	79·2	126·0	76·8	118·0	10·17	10·21	65·3	99·6
Same as Experiment 3 ..	4*a*	200	79·2	126·0	90·7	118·0	—	10·21	77·3	—
	4*b*	200	76·2	120·0	90·0	115·3	10·04	10·21	79·3	98·5
Same as Experiment 3, but different sample ..	5*a*	180	68·8	126·0	84·4	102·5	—	10·21	82·2	—
	5*b*	180	68·8	128·0	82·6	—	—	10·21	80·7	—

(*a*) Nitrogen determinations were made under the direction of Mr. W. C. Cope, of the Explosives Laboratory of the Bureau of Mines. Analyses were made by Mr. Cope's modification of the Kjeldahl method, which has been devised for nitro substitution products. (Description about to be published). The modification is characterised by a preliminary twelve-hour cold digestion of the unknown substance with sulphuric acid, salicylic acid, and zinc dust.

Table II.—*Trinitrotoluene from Mononitrotoluene.*

First Stage.—Mono- to dinitro toluene (acid specified).			Per cent excess acids.	*Second Stage.*—Di- to trinitrotoluene.. (Acid in excess of amount specified).								
				Hours heated at temperature (°C.)—						Yield.		Melting-point (°C.)
Exp. No.	Heated. Hrs.	Temp. (°C.).		95.	100.	110.	115.	120.	130.	Grms.	Per cent.	
1.	1	88	0	1	1½	0	0	0	0	64	57	−72
2.	1	88	0	1	1	0	½	0	0	61	58	−69
3.	1	88	0	1	1½	½	0	½	½	61	55	−72
4.	½	115	0	1	0	0	0	1½	0	60	69	−77
5.	½	115	25	1	1½	1	0	½	0	60	73·5	−77·5
6.	½	115	25	1	0	0	0	1½	0	58	75	−79
7.	1	115	50	1	1½	0	0	0	0	60	74	−80
8.	1	115	50	1	1½	0	0	0	0	56	75·5	−79·5
9.	1	115	50	1	1	0	0	0	0	60	75·5	−79
10.	½	115	50	1	0	0	0	1½	0	60	78	−79·5

(*a*) melting-points were determined under the direction of Mr. Cope in the Explosives Laboratory of the Bureau of Mines. Thermometers were carefully standardised. The apparatus was that described by Mulliken, "A Method for the Identification of Pure Organic Compounds," 1908, i., 218.

in the liquid), and with a short condenser, through which is passed a motor-driven stirrer. The nitrating acid is introduced through the condenser, being run in from a dropping funnel.

For each 100 grms. of toluene a mixture of 110 grms. of nitric acid (sp. gr. 1·456) and 143 grms. of sulphuric acid (sp. gr. 1·84) is required (the mixture made up in these proportions is hereafter designated as "mixed acid"). In the process of nitration the cold mixed acid is run in slowly from the dropping funnel. During the main course of the reaction the temperature is not allowed to rise above from 45° to 55°. At the end, when the concentration of excess acid is small, the mixture is heated to 100° in order to complete the nitration. It is claimed that by this method it is possible to obtain a yield which is 95 per cent of the theoretical.

After completing the process of nitration the mixture is cooled, and then washed with water to remove the remaining acid. The resulting oil is dried and distilled *in vacuo*. The use of vacuum or steam in the distillation does not permit the obtaining of actual boiling-points, but there is no necessity for this. A low boiling fraction comes over first, which includes the paraffins and any small residue of unnitrated toluene. The thermometer then starts to rise rapidly, and at this point the receiver is changed. After the collection of a large fraction the temperature begins another sharp rise, and the distillation is then stopped. The residue consists of resins and any di- or trinitrotoluene which may have been formed.

The experiments with mononitrotoluene were conducted to ascertain:—

1. The effects of various methods of preliminary deolefinisation.
2. The effect of variation in the quantity of nitrating acid upon the degree of purity.
3. The quantitative yields of the samples of mononitrotoluene obtained.

Details of these experiments are given in Table I. In Experiment 2, the sample of the toluene mixture was deolefinised by treatment with quantities of 10 and 5 per cent of its volume of ordinary concentrated sulphuric acid. The product was washed with water and alkali, dried, and redistilled. A fraction was collected, boiling between 105° and 110°. This represented 75·2 per cent of the original, and, on the approximately correct assumption that no toluene was lost in the preliminary treatment, it contained 97 per cent of actual toluene.

In Experiment 3 the sample of the toluene mixture was deolefinised as in Experiment 2, but the resulting mixture was nitrated immediately after drawing off the second lot of acid sludge.

Experiments 1, 2, and 3 established without any possible doubt the fact that by the simple process of nitration to the mono-stage, with subsequent distillation, it is possible to get rid of the impurities which are associated with aromatic hydrocarbons produced by the cracking of petroleum. The products obtained are pure within the limits of errors of analysis.

Correct indications as to the desirable method of preliminary treatment were obtained only by careful interpretation of results. It appears on superficial examination of the data obtained that the most desirable method on the basis of percentage yield is that which involves purification after the preliminary treatment with sulphuric acid. This is, however, undesirable from a commercial point of view. Mechanical difficulties arise on account of the formation of emulsions, and, in addition, this treatment is unnecessary, since the acid removed is immediately added again when the nitrating "mixed acid" is run in.

The next best yield was obtained when there was no preliminary treatment, and this result furnished the key to a solution of this phase of the problem. The quantity of mixed acid used was calculated for 100 grms. of actual toluene, and as this amount of aromatic hydrocarbon was not present there was some conversion to dinitrotoluene, which substance is in the present course of procedure lost in the residue after distillation. When the preliminary deolefinisation was omitted some of the nitric acid was taken up by the unsaturated bodies and the excess reduced, which resulted in an increased yield of mononitrotoluene. From a commercial point of view this is an undesirable mode of procedure, since it involves allowing expensive nitric acid to do work which may be performed equally well by cheap sulphuric. It is obvious, however, that the magnitude of the yield is controlled by this factor of acid concentration, and it appears that an excess is undesirable from the point of view of yield of the desired product as well as cost of wasted nitric acid. The conditions of preliminary treatment seem to have no effect upon the purity of the product, the general method of procedure being such as to fix this at a high mark.

On the basis of general considerations of expense and convenience the process involving a simple refining with sulphuric acid and no intermediate washing before nitration seemed most desirable, even in face of the fact that it seemed to give lower yields than either of the two other methods. The low yield appeared to be explainable on the basis of excess of nitrating acid, and Experiments 4*a* and *b* were therefore conducted to demonstrate whether or not this was the case. The indications furnished by these two experiments were clear-cut and satisfactory. To show that there was nothing accidental about them, and that they were not characteristic of the particular sample of toluene mixture used as original material, some supplementary preparations (Experiments 5*a* and *b*) were made, using a second sample of toluene, which had a lower content of the aromatic hydrocarbon. The quantity of acid used was equivalent to that needed for 71 grms. of toluene, so that a 3 per cent excess was present.

Conclusions regarding the Preparation of Mononitrotoluene

1. Mononitrotoluene of a high degree of purity may be prepared from the paraffin-olefin-toluene mixtures obtained by the simple distillation of cracked petroleum. The purity of the nitro-product and, consequently, its utility for the preparation of water-washed trinitrotoluene, is fixed by the general method of treatment, which ensures a very sharp separation of mononitrotoluene from the impurities associated with it.

2. It is desirable to remove olefins by a preliminary extraction with sulphuric acid. Otherwise they consume expensive nitric acid and incidentally develop so much heat that the process of nitration is difficult to regulate. No washing is necessary between the processes of deolefinisation and nitration, since such a treatment removes acid which must be added again as soon as nitration is begun.

3. The quantity of nitrating acid mixture should be based approximately on the actual toluene in the mixture to be treated and not on the total quantity of the latter. An excess of acid causes the formation of dinitrotoluene, which under present conditions is an undesirable occurrence.

Preparation of Trinitrotoluene.

Experiments on the preparation of trinitrotoluene were not conducted for the purpose of modifying or improving any of the numerous methods which have already been proposed. The work done was for the simple purpose of obtaining absolute verification of the results obtained by the analyses of the samples of mononitrotoluene prepared by the method indicated above. The fact to be established was that the fraction of a per cent of impurities included in the mononitro product did not in any unexpected way interfere with its transformation into water-washed trinitrotoluene of a satisfactory degree of purity.

Preliminary experiments were performed according to various sets of directions found in the literature, but the products obtained invariably melted below the required mark of 75° C. A satisfactory product could always be obtained by a simple crystallisation from alcohol, but this fact was of little significance.

It finally appeared necessary to concentrate on the details of some specific method, and for this purpose the poly-stage process employed by one of the large explosive companies in this country was selected as most promising. Translated into terms of quantities useable in the laboratory the method of procedure is as follows:—

First Stage—Transformation of Mononitrotoluene into Dinitrotoluene.

Amount of mononitrotoluene	50 grms.
Acid concentration	107·6 grms. of a mixture of 1 part by weight of HNO_3 (sp. gr. 1·5) and 2 parts H_2SO_4 (sp. gr. 1·84).
Temperature during addition of acid	88·0° C.
Time of heating	½ hour at 88·0° C.

The mixture is then cooled and the spent acid drawn off.

Second Stage—Transformation of Unpurified Dinitrotoluene into Trinitrotoluene.

Acid concentration	67 grms. of "oleum" (fuming sulphuric acid containing an excess of 20 per cent of SO_2 over ordinary conc. H_2SO_4). 42 grms. of nitric acid (sp. gr. 1·5).
Temperature during addition of acid	Below 88·0° C.
Heating	1 hour at 88·0°. 1½ hours at 100°.

The mixture is then cooled and the acid drawn off. The remaining product is washed several times with hot water, being stirred with the latter while in a molten condition. It is finally dried.

The first experiments were performed using the quantities of acids specified in these directions but with modifications in the time and degree of heating (Nos. 1 to 4, Table II.).

This series of experiments was instructive, since it appeared that no improvement could be secured through increasing time of heating and temperature in the second stage of the process. A marked improvement, however, appeared by the modification of treatment in the first stage. Heating for one-half hour at 115° instead of an hour at 88° resulted in an increase of about 10° in the melting-point of the product.

The next series of experiments involved a 25 per cent increase in the amount of acid used for the second stage of the nitration (Nos. 5 and 6, Table II.). An improvement was shown here, the product obtained in one case being just above the satisfactory degree of purity.

From a commercial point of view there seems to be no inherent objection to the employment of a considerable excess of acid at the second stage of the reaction, since the spent acid may be utilised in an earlier stage in the next cycle. Hence, instead of proceeding with experiments involving a 25 per cent excess of acid, the quantity was increased to a 50 per cent excess, and a third series of preparations made (Nos. 7 to 10, Table II.). Three of these four experiments yielded satisfactory products, and there seemed to be no doubt but that with the higher concentration of acid there was little difficulty in producing a trinitrotoluene of a satisfactory degree of purity. The yields were all in the neighbourhood of 60 grms., which is about 70 per cent of the theoretically possible amount. This is of course low for commercial work, but conditions here were less favourable than they would be on a large scale, and, at best, the work has only remotely approached completion in the matter of determining optimum conditions for the process of nitration. Here as well as in the earlier part of the work, attention was given only to the establishment of general principles, and no attempt was made to learn details.

Conclusions regarding the Preparation of Trinitrotoluene.

1. Trinitrotoluene, of a satisfactory degree of purity, may be prepared from the mononitrotoluene obtained by the nitration of the toluene-paraffinolefin mixtures produced by the fractionation of "cracked" petroleum.

2. From the laboratory point of view, at least the polystage process seems best. The transformation from mono- to di-product should involve a fair degree of heating and a moderate concentration of acid. The final stage of the nitration should be conducted with a considerable excess of strong acid, which acid need not be wasted, since when drawn off it may be used in an earlier stage of the next cycle of nitration.

General Summary.

I. The aromatic hydrocarbons produced by the "cracking" of petroleum may be utilised for the preparation of nitro-products without being brought to a high degree of purity. The foreign substances not easily removable are paraffins, and these are not affected by reagents of sufficient vigour to transform the aromatics quantitatively into mono-nitro products. These compounds may be separated in a high degree of purity by a simple process of distillation.

II. The mononitrotoluene prepared by the method indicated may be readily converted into trinitrototoluene which, when washed with hot water, satisfies the ordinary commercial specification of a melting-point of 75° C.

REPORT TO THE GOVERNORS OF THE HUDDERSFIELD TECHNICAL COLLEGE CONCERNING THE DEPARTMENT OF COAL-TAR COLOUR CHEMISTRY.

Gentlemen,—In June last you announced your decision to establish in Huddersfield a Department that should devote itself to Post-Graduate and Research work in matters connected with the coal-tar colour industry. A Department that should produce the highly-trained technical chemists required by the coal-tar colour industry and become the national centre for specialised teaching and research in all chemical matters affecting that industry.

Of the need for such an institution there is overwhelming evidence and, for the attainment of the objects in view, the town of Huddersfield is, and ought to remain, the most suitable place for the erection of such a national institution as it is your desire and determination to raise up.

The equipment of our temporary laboratories placed at our disposal by the chemical department was sufficiently forward for work to commence in September, but, though the best has been made of the space available, the interest shown in the matter has been so great that the laboratory and lecture room space is already overcrowded, and no time should be lost in completing arrangements for the erection of the new buildings for the department, for which such an admirable site has been obtained, and sketch plans already drawn up. This is the more urgent in view of the fact that the carrying through of a great proportion of our work is utterly impossible in our present buildings. In the meantime, arrangements are being made to give temporary accommodation for further workers in the department.

Not only is teaching work proceeding, but important research work is also in progress in the department.

The manner in which the various firms connected with the coal-tar colour industry, both in and outside Huddersfield, have interested themselves in the undertaking and given very valuable assistance, is exceedingly encouraging, and your decision to appoint as head of the department one who is not, in any way, tied by appointment to any particular firm, has in no small degree been responsible for this. This decision will also greatly assist in attaining to your original aim—the establishment in Huddersfield of a laboratory for research and post-graduate work that shall be the national centre to which *all firms* connected with the coal-tar colour industry shall naturally come for assistance, and around which all matters connected with coal-tar colour chemistry shall centre.

The completing of arrangements for the new buildings, which when erected will contain a very fine set of laboratories—by far the finest available in any educational institution for coal-tar colour chemistry in this country, and the extension of the scope of the department's library on a scale compatible with such a national scheme, are matters of great urgency and importance, and they are receiving the necessary attention that no delay shall occur when the funds required become available.

The provision of research scholarships tenable in the department has received much attention, and a fund for their endowment is already in being, which, however, needs to be greatly increased, so that a really comprehensive scholarship scheme may be put into operation.

(Signed) Arthur E. Everest, D.Sc., Ph.D.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 27, 1916.

Mr. E. F. Smith, A.R.C.Sc., Vice-President, in the Chair.

A paper entitled "*The Application of the Kerr Effect to the Determination of the Saturation Values for Magnetism of Ferro-magnetic Metals, Compounds, and Alloys,*" by S. G. Barker, D.I.C., Ph.D., was read, in the absence of the author, by Dr. S. W. J. Smith, F.R.S.

The paper describes work carried out in the laboratory of Prof. Du Bois on the relation between the intensity of magnetisation of various ferro-magnetic materials, and the rotation of the plane of polarisation of plane polarised light reflected from a polished surface of the material. The specimens, in the form of circular discs 5 mm. in diameter and 0·5 mm. thick, were soldered to one of the pole pieces of a large electro-magnet. Through an aperture in the other pole, monochromatic light, polarised in two nearly coincident planes by means of a Lippich polariser, was incident almost normally on the polished surface of the specimen. The reflected beam passed through an analyser, the rotation of which could be measured, by means of an auxiliary optical system, to a high degree of accuracy.

In the first part of the paper results are given for a number of materials of known magnetic properties in order to establish the validity of the method, due to Du Bois, of obtaining the value of the saturation intensity from the curve connecting field strength with rotation. The method is then applied to materials of unknown properties. The variation of the Kerr constant with the wave-length of the light was also determined for a number of substances.

Discussion.

Mr. D. Owen asked if the paper, in addition to establishing the view that the rotation was proportional to the intensity of magnetisation, brought forward any new results that were useful to theory. For instance, he recollected a paper by B. Hopkinson, in which it was found possible to obtain an intensity of magnetisation greater than that obtainable with pure iron, and he noticed that in the present paper there was an alloy of iron and cobalt which exceeded pure iron in saturation intensity. Was it now taken for granted that it was possible in an alloy to obtain magnetisations greater than that of either component, or were the results in the paper somewhat novel in this respect?

Dr. Smith said that saturation intensities of magnetisation were of importance for various reasons. For instance, as Weiss had shown, it was of theoretical interest to know their temperature variations. Again, in the case of a "mechanical" mixture of two substances, the saturation intensity would be related in a simple manner to those of the constituents. There was much evidence that annealed steels are mixtures of iron and iron carbide. Hadfield and Hopkinson, in the paper which had been mentioned, had shown that the saturation intensities of magnetisation of such steels were compatible with this view, and had deduced a value for the saturation intensity of the carbide. It would have been of interest if Dr. Barker had determined the latter directly, as had been his intention, before the work was interrupted. Alloys were not, however, always simple mixtures. The steel examined by Hopkinson and Hadfield to which Mr. Owen had referred, was a nickel steel, and its total magnetisation was greater than the sum of those which its constituents would have exhibited separately, although it was not as great as that of pure iron. The reason probably was that nickel-iron alloys form solid solutions (mixed crystals) instead of mechanical mixtures. The same is probably true of cobalt-iron alloys, although in this case a material can be obtained (possibly a compound) whose saturation magnetisation is actually greater than that of pure iron. It had been proposed to use this alloy commercially. Other solid solutions were known in some of which the magnetisation was greater, and in others less, than that which mechanical mixtures of the components would have exhibited.

A paper entitled "*The Influence of the Time Element on the Resistance of a Solid Rectifying Contact*" was read by Mr. D. Owen, B.A., B.Sc.

The resistance of a solid rectifying contact, and consequently the exact shape of the resistance characteristic, depends upon the time for which the testing current is allowed to flow. A series of characteristics are given corresponding to durations of contact extending over a the range one forty-thousandth of a second to thirty seconds. The following conclusions are drawn:—

1. That the variation of resistance with voltage may be attributed entirely to thermal effects.
2. That the characteristic obtained by applying the testing voltage for one hundredth of a second is, at moderate voltages, materially the same as that which would be found at the expiry of a period of the order of a millionth of a second.
3. That the sensibility of a wireless receiving circuit (in which the rectifying contact is used) does not differ very appreciably from that deduced from a slow period characteristic.
4. That an important fraction of the contact-resistance resides in a stratum of molecular thickness at the interface of the two elements of the contact, and that it is in this region alone that rectifying action at very high frequencies is effected.

Discussion.

Prof. G. W. O. Howe thought the experimental method of Mr. Owen was the correct way to tackle the problem of high frequency phenomena, and was preferable to taking oscillograph records at low commercial frequencies, and attempting to deduce from them what will happen at very much higher frequencies. What is the limit to the number of times per second that the ball may be struck for the results still to apply to one impact only? From one point of view the results were disappointing, inasmuch as it had been necessary to introduce a mysterious stratum of molecular thickness, and the problem arises as to what these layers consist of; what are their properties, and why is the thermal effect largely confined to them?

Dr. H. S. Allen asked if any attempt had been made to remove surface films from the contacts. Prof. Milliken had recently obtained very simple results in photoelectricity by working in a high vacuum, so as to remove all films of moisture. Could this not be done in Mr. Owen's experiments?

Dr. Eccles said that the subject of contact resistance was of wide importance, apart from its application to electric wave detectors. It had been investigated by Wheatstone and Heaviside in other connections—microphones, for example. It was important also in connection with the contacts at dynamo brushes. There had always been a desire in wireless telegraphy circles for high-frequency characteristic curves. Doubtless, if oscillograph records could be obtained for frequencies of 10^{-6} second, they would be very like what Mr. Owen gets by his point to point method. He would have been glad if the author had tried similar contacts—*e.g.*, two carbons, two galenas, or even two metals. In these cases there would be no thermo-electric phenomena to confuse the issue. He was not convinced on the question of the molecular layer. The author states that "in actual practice the mean diameter of the area of a good rectifying contact is, as a rule, far greater than 10^{-4} cm." Now, if one pictures a piece of metal resting on the zigzag surface of a crystal, it is obvious that actual contact will only occur at points and ridges, and it is surely impossible for anyone to assert what the order of the area of contact is. He preferred to think that the effects were due to the heating of the surface layers of the stuff, due to concentration of the current flow into the narrow regions where actual contact exists. Usually the harder the crystal the better the rectification obtained, due possibly to the greater concentration of current in the smaller and sharper contact points. He thought perhaps too much stress was laid on the high-frequency characteristic. When an oscillation passes through the contact of a crystal touching a metal plate it is the after effects of the heat developed which produce the thermo-electric currents that affect the telephone. Therefore, while of scientific interest, the high-frequency characteristics are not very essential from the point of view of wireless telegraphy.

Mr. F. E. Smith thought Dr. Allen's suggestion a valuable one. About fourteen years ago a paper was read to the Society showing that films of liquid remained attached to solids even up to temperatures of 300° C.

Mr. Owen, in reply to Prof. Howe, thought there was no mystery connected with the contact layer. We cannot assume complete continuity of material at a contact, as in a weld, since there is never any difficulty in pulling the elements apart. With respect to the repeated impacts, the time between the impacts was never less than about 8000 times the duration of contact. The point raised by Dr. Allen required investigation. It was scarcely necessary for him to reply to most of Dr. Eccles' remarks, as they really constituted an independent contribution to the subject.

On account of the lateness of the hour, Mr. B. W. Clack kindly agreed to postpone the reading of his paper "On Diffusion in Liquids" until the next meeting.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, Nov. 1, 1916.

Mr. George Embrey, President, in the Chair.

A certificate was read for the first time in favour of Mr. Gerrard W. Baker.

The following papers were read:—

"*Quantitative Microscopy.*" By T. E. Wallis, B.Sc. (Lond.), F.I.C.

Quantitative results based on microscopical work have hitherto failed to obtain recognition such as is accorded to similar results based upon chemical processes. By adopting the procedure outlined below, the author shows that a high degree of precision can be given to quantitative work with the microscope, which has a unique value in those instances where chemical methods are inapplicable. Equal weights of the material under investigation and of a standard mixture for comparison, are separately mixed with similar weighed quantities of lycopodium spores. The mixed powders are suspended in a suitable fluid, and two slides are prepared from each suspension. Ten fields, selected according to a pre-arranged plan, are counted on each slide, and the average ratio of the number of particles of the substance to be determined to the number of lycopodium spores present is found, and reduced in each case, to the number corresponding to 100 lycopodium spores. The figures so obtained are proportional to the quantities of material present in the substance and in the standard mixture respectively. A simple calculation gives the quantity sought.

The accuracy and utility of the method is shown by experiments with typical mixtures, including wheat-flour, potato-starch, and mustard, each mixed with cornflour; wheat-flour containing potato-starch; white pepper adulterated with ginger and with rice-starch; and gentian root with added coconut shell.

"*Note on an Interpolation Formula for transforming Scale Divisions on the Zeiss Butyro-Refractometer into the corresponding Refractive Indices.*" By C. C. Roberts, M.A., A.I.C.

With the directions for using the butyro-refractometer a table is given showing the refractive index for sodium light for every tenth division of the scale.

The following formula will be found to give accurately the refractive index corresponding to any given scale reading and can be used for intermediate scale readings: = If n_D be the refractive index for sodium light, and x the scale reading. Then—

$$n_D = \frac{1422 + 0{\cdot}817\,x - 0{\cdot}00142\,x^2}{1000}$$

A "*Criticism of Vaubel's Bromine Values.*" By Cecil Revis and H. R. Burnett.

Vaubel's method of estimating total bromine values leads to concordant results when using the same oil, but the figures do not appear to bear the same relation to the true iodine value as stated by Vaubel.

The primary bromine value does not appear to be the distinct stage in the bromine absorption which Vaubel asserts is the case, and possibly only marks a point at which the speed of bromine absorption appears to rapidly decrease.

Institution of Mining and Metallurgy.—In place of the usual Ordinary General Meeting, an Informal General Meeting of the members will be held, by kind permission, at the Rooms of the Geological Society, Burlington House, Piccadilly. W., on Thursday next, November 16, at 5.30 p.m.

NOTICES OF BOOKS.

The Right Honourable Sir Henry Enfield Roscoe, P.C., D.C.L., F.R.S. By Sir Edward Thorpe, C.B., F.R.S. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, & Co. 1916. Pp. viii. + 207. Price 7s. 6d. net.

Although Sir Henry Roscoe has left behind him a volume of reminiscences which gave a very full account of his career and experiences, and left very little untold that he himself could tell, this biographical sketch by a pupil, and afterwards highly esteemed collaborator, will be none the less welcomed by scientific men, for Sir Edward Thorpe can present his subject from many different points of view and can pass an admirable judgment upon Roscoe's powers and achievements. Much space is given to an account of the early history of Owen's College, which owed a very great debt to Roscoe's energy and administrative ability, and of the Yorkshire College and the foundation of the Victoria University in which Roscoe took a leading part. He was possessed of a very clear insight into the needs of the student, and especially of the science student of his time, and was able to throw much light upon some of the educational problems of his day, the vigour of his intellect and the boldness of his views often finding solutions which might have escaped a more hesitating and timid man. As a teacher he was inspiring and invigorating, and as an author he met with extraordinary success, his "Lessons in Elementary Chemistry" having been perhaps more widely used than any other work of the same size and scope, while his "Chemistry Primer" was translated into Icelandic, Polish, German, Italian, Japanese, Bengali, Turkish, Malayan, and Tamil. Sir Edward Thorpe has rendered a notable service to science in publishing this sketch, and in making more widely known the activities of a man of science whose intellectual power was so admirably combined with practical and business ability.

Five-Year Course in Chemical Engineering. Massachusetts Institute of Technology. Cambridge, Massachusetts. 1916. Pp. 8.

A Master's Course in Chemical Engineering. Reprinted from the *Journal of Industrial and Engineering Chemistry*, August, 1916, Vol. VIII., No. 8, page 746.

The scheme which is outlined in these two pamphlets appears to be so likely to be attended by valuable results that it is undoubtedly deserving of the most careful consideration by educational experts in this country. Some destructive criticisms may perhaps be levelled against it and in some details it will probably be found to require modification, but it certainly represents a step in the right direction, and the students who are able to take advantage of it will be fortunate. The directors of the Institute recognise that the man who is going to make a successful chemical engineer must possess not only a sound scientific knowledge of the chemistry and physics of materials and processes employed in the chemical industries, but must also have had some opportunity of acquiring a first-hand knowledge of large scale operations, and of applying himself to the study of some of the unsolved problems of the industries. With the aim of thus training its students the Institute has arranged a five-year course in chemical engineering, of which the following details will be of interest. The course for the first three years and the first term of the fourth year includes English, chemistry, mathematics, physics, German, machine drawing, and some engineering, besides some subsidiary subjects. At the conclusion of the first term of the fourth year suitable students will be allowed to enter the new school of chemical engineering practice, where they will remain for about seven months. This school will be carried on at five centres, namely, at Bangor, Maine, at the plant of the Eastern Manufacturing Company, makers of electrolytic caustic soda and calcium hypochlorite, cellulose from wood, bond and ledger papers. Secondly at Everett, Mass., at the plant of the New England Gas and Coke Company, makers of gas, coke, ammonia, and tar by-products. Thirdly at Niagara Falls, N.Y., at the plant of the Carborundum Company, makers of carborundum, silicon, and other electric furnace products. Fourthly at Stamford, Conn., at the plant of the American Synthetic Colour Company, makers of phenol, picric acid, dye-stuffs, and coal-tar intermediaries. Fifthly at Northampton, Pa., at the plant of the Atlas Portland Cement Company, makers of Portland cement. Groups of the students will visit these centres in turn remaining six weeks at each, so that after thirty weeks each student will have been to each centre. The stations will be in the charge of resident members of the Institute Faculty, and will be properly equipped with testing laboratories, lecture rooms, libraries, &c., for the use of the students, who will be thoroughly instructed in the details of the practice and processes at each centre. They will learn something about methods of factory control, costs of manufacture, &c., and—perhaps the most valuable outcome of the scheme—will get suggestions for advanced research work. At the expiration of the year they will return to the Institute for their last year's work, when opportunity will be given them for specialising and doing original work in any branch which they may have found interesting. Upon the completion of the course the degrees of Bachelor of Science and Master of Science will be awarded. As a return for the use of the factories for the students the Institute will establish a research organisation for each company, which will devote itself entirely to the study of the special problems of the factory, and the Faculty of the Institute will function as a consulting staff. The value of this co-operation is obvious and the scheme appears to be thoroughly well planned. The time spent by each student at the different stations might be found inadequate, and it might be better to limit the number visited by each student so as to give him a better chance of obtaining a real insight into factory conditions, or, better still, devote a whole year to the period of factory training. Some details of the curriculum might also be altered with advantage, but on the whole there is very little to criticise, and further information about the scheme and accounts of its working will be awaited in this country with much interest.

Eclipse or Empire? By Herbert Branston Gray, D.D., Oxon., and Samuel Turner. London: Nisbet and Co., Ltd. 1916. Pp. x. + 316. Price 2s. net.

The aim of this book and the spirit in which it is written are alike excellent, and it is much to be hoped that the valuable lessons to be learnt from it will be taken to heart by the public. Although written in no bigoted spirit, but on the contrary with moderation and restraint, it seems not improbable that the authors will be accused of exaggeration by those comfortable theorists who believe that true patriotism involves a blind belief in the unassailable supremacy, both in the past and in the future, of British methods. But the men who are doubtful whether all is entirely with us (and fortunately they form no inconsiderable part of the population now), and all who have a genuine desire to think independently and sanely, will owe the authors a debt of considerable magnitude for their plain speaking, their fervid patriotism and fearlessness. In their opinion the root evil, which is the cause of Great Britain's decay as a Power, is the lack of a proper system of national education, and they believe that we are doomed to become a second-class power in the very near future unless we modify our ways, and this even if we win the war. The aim of the book is more to point out the existence and the growing seriousness of the evils than to suggest the actual remedies to be applied, but at the same time definite and thoroughly sound and practical criticisms of present methods of education are made, and a scheme for reform is outlined. The authors recognise that scientific facts must be known more widely and more thoroughly if the sons of the British Empire are to prove worthy of their inheritance, and without showing any want of a sense of proportion they make it clear that they consider that the curriculum of British schools of all grades must be very drastically altered. Equally strongly they urge that the adoption of a slavish imitation of Germany's methods would be disastrous in England. The necessity for adding to our knowledge of our Dominions beyond the seas and benefitting by that increased knowledge is emphasised, and a stirring appeal is made to the patriotism and courage of all English men and women whatever their status in society. One of the most valuable and arresting parts of the book is the glossary, which consists of short reviews of the state of various trades and industries in Great Britain. These reviews have been prepared by men actually engaged in the industries, and they contain dispassionate expressions of their opinions as to their history and present condition. In every respect they bear out the authors' contention that "during the last twenty to forty years most of the inventions, new ideas, and developments have been given to the world by countries other than our own; furthermore, that their value has been more quickly appreciated and put to practical use in foreign lands," and the evidence of the seriousness of our position is overwhelming.

MISCELLANEOUS.

Royal Society of Arts.—On Wednesday, November 15, at 4.30 p.m., the Opening Address of the 163rd Session of the Society will be delivered by Dr. Dugald Clerk, F.R.S., Chairman of the Council. The subject of the Address will be "The Stability of Great Britain."

Proposed Memorial to the late Dr. S. P. Thompson. —A meeting of the Guarantors will be held at the Institution of Electrical Engineers at 5 p.m. on Thursday next, November 16, to receive a report from the Preliminary Committee and to decide on future action.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., the Duke of Northumberland, K.G., President, in the Chair. Dr. H. E. Armstrong, Ph.D., F.R.S., was elected a Manager in place of the late Prof. S. P. Thompson. Resolutions of thanks were passed to Richard Pearce, Esq., for his donation of £100, and to John Y. Buchanan, Esq., for his donations of £100 to the Fund for the Promotion of Experimental Research at Low Temperature and of £100 to the General Fund. Lord Glenconner and Sir William Trollope, Bart., were elected Members. A Resolution of Condolence with the relatives of the late Sir Victor Horsley, a Member of the Royal Institution, was passed.

MEETINGS FOR THE WEEK.

Wednesday, 15th.—Royal Society of Arts, 4.30. "The Stability of Great Britain," by Dr. Dugald Clerk.

— Microscopical, 8. "The Microscopic Work of the Accademia dei Lincei," by C. Singer. "A New Tank and Pond-weed Holder for Use with Greenough Immersion Objectives," by S. C. Akehurst.

Thursday, 16th—Institution of Mining and Metallurgy, 5.30. (Informal General Meeting).

— Chemical Society, 8. "A Simple Method of Estimating Arsenic in Organic Derivatives," by A. J. Ewins. "New Method for the Preparation of Nitrosyl Tribromide," by R. L. Datta and N. R. Chatterjee. "Neutral Potassium Persulphate as a Reagent in Organic Chemistry," by K. L. Datta and J. N. Sen. "Hydrolysis of Iron Ammonium Alum," by W. N. Rae.

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COLOUR STANDARDS AND COLORIMETRIC ASSAYS.*

By H. V. ARNY and C. H. RING.
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Introduction.

Entrusted by the Committee on Revision of the National Formulary with the task of standardising the colouring agents, cudbear and caramel, recipes for tinctures of which are given in that book, one of us (in 1908) became interested in colour standardisation. Finding that no rational system of colour-matching obtained other than the Lovibond tintometer, the standard glasses of which are arbitrarily chosen, study suggested the use of a standard red solution made from a cobalt salt, a standard yellow solution made from a ferric salt, and a standard blue solution made from a copper salt. Such solutions were prepared, and by mixing the three, blends were obtained that gave a variety of hues limited only by the character of the colours of the original fluids. This line of coloured fluids, the "Co-Fe-Cu" blends—which were demonstrated and described at the Eighth International Congress of Applied Chemistry (see *Proceedings*, xxvi., 319)—gave a fine line of green, yellow, and orange shades, but were lacking in deep blues and reds, so further work (Arny and Pickardt, *Druggists' Circular*, 1914, lvii., 131) was performed in 1913 and during the past year by the present writers. The result of this work was the preparation of a supplemental set of colours, designated as the "Co-Cro-Cu" blends, which furnish the needed blues and soma of the reds. To secure the purplish reds blends of volumetric solutions of potassium dichromate and of potassium permanganate have been devised, as indicated in Table I. These two lines of coloured fluids are described at length in the *Journal of the Franklin Institute* for August, 1915, p. 199. Some of the matches obtained by the use of these solutions are given in Table II. The blending of the acidulated fluids or of the ammoniacal fluids can of course be performed in any proportion that fancy suggests.

Nomenclature.—The original red fluid is "R.Y.B., 12—0—0;" the original yellow is "R.Y.B., 0—12—0;" and the original blue is "R.Y.B., 0—0—12." The sample designated as "R.Y.B., 6—6—0" will of course be an orange hue; that called "R.Y.B., 0—6—6" will be green, while "R.Y.B., 6—0—6" has a purplish tint. That the intensity of the three basic fluids is about the same is shown by the fact that "R.Y.B., 4—4—4" closely approaches, both in the "Co-Fe-Cu" and in the "Co-Cru-Cu" series, the "neutral grey," which is the closest that blended reds, yellows, and blues can approach to water-white condition.

Permanency of Fluids.—The original acidulated cobalt, iron, and copper solutions and their blends neither fade nor precipitate to a percepible degree until at least two years old; the ammoniacal cobalt and chromium solutions have now been under observation for over a year without any fading being detected. The ammoniacal copper, on the other hand, precipitates, and consequently undergoes colour change within a few weeks, but our experiments so far show that the blends keep satisfactorily when sealed in ampuls or kept in well filled rubber-stoppered bottles, which are not opened. In practice, however, the ammoniacal copper solution is prepared by diluting the permanent N/2 acidulated copper solution to N/50 strength by the addition of ammonia water and water; hence the preparation of the "Co-Cro-Cu" blends is merely a matter of mixing solutions that can be kept in stock for months without deterioration.

Use of Coloured Fluids in Colorimetric Assays.

The article in the *Druggists' Circular* mentioned above showed that the prescribed methods of colorimetric assays were far from perfect. This year, however, we are able to report that practically every tint desired in colorimetric work can be obtained from either the "Co-Fe-Cu," the "Co-Cro-Cu," or the "Cro-Manganate" blends, and that under certain conditions the colorimetric assays themselves can be made uniform.

Cautions.

Unless a colorimetric assay is performed with proper regard to the amount and proportion of the reagent employed, the test is very liable to be inaccurate when the colour is matched against a solution containing a known quantity of the substance under examination, and it is practically worthless when matched against a rigid standard of either coloured glass or coloured fluids unless this fact is understood. The data given further along show that:—(1) In some cases a difference of only a few drops of the reagent may make a vast difference in the colour of the two samples, each having the same volume and the same amount of substance under assay; (2) several lots of a given reagent, made by slightly different recipes, may fail to produce uniform colour results, even though exact duplication of work is performed in each test (*e.g.*, Nessler's solution).

On the other hand, if the reagents are carefully prepared, and if the test itself is carried out with proper regard to the exact quantities of the reagents and to the sequence of mixing, the colour results are as a rule uniform. This also holds good in regard to different samples of the chemical being used, provided of course that only chemicals of tested purity are employed. Such being the case, our plan of colour standardisation is shown to be entirely feasible, and its use will greatly facilitate colorimetric assays by obviating the preparation of standard solutions of the chemicals under assay.

Ammonia Colorimetric Tests.

Four different recipes are available for the preparation of Nessler's reagent, the universally recognised method for the determination of ammonia in minute quantities. (The recipes were obtained from the following books:—(1) "The United States Pharmacopeia"; (2) "Standard Methods for the Examination of Water and Sewage," American Public Health Association; (3) "Examination of Water," William P. Mason; (4) "Sanitary and Applied Chemistry," E. H. S. Bailey). These four recipes differ only in the proportional amounts of the ingredients and the manner of mixing them. In another recipe, suggested by Frerichs and Mannheim (*Apoth. Zeit.*, 1914, xxix., 972), mercuric iodide is used in place of mercuric chlorides in the preparation of this reagent. We tested each of these reagents on standard samples of ammonium chloride solution prepared from "Kahlbaum-Reagent-Ammonium Chloride," following the usual method of adding 2 cc. of the reagent to 50 cc. of the solution containing a known quantity of nitrogen in the form of ammonia. The strikingly discordant results obtained are shown in Table III.

Besides the six different Nessler solutions used in Table III., we also used a solution prepared according to the U.S.P., but made up freshly. A precipitate formed at every trial, just as when solutions made by the Mason or Bailey recipes were used.

It is of course well known that an "aged" Nessler solution, at least six months old, should be used when

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* From *Journal of Industrial and Engineering Chemistry*, viii., No. 4.

TABLE I.—*Solutions Used for Making Standard Blends.*

Name of series.	Colour.	Substances used.		Solvent used.	Strength of solutions.
		Formula.	Grms.		
"Co-Fe-Cu"	Red	$CoCl_2.6H_2O$	59·49	1 per cent hydrochloric acid (*a*)	N/2
	Yellow	$FeCl_3.6H_2O$	45·05		
	Blue	$CuSO_4.5H_2O$	62·43		
"Co-Cro-Cu	Red	$CoCl_3.5NH_3.H_2O$	2·7	2 8 per cent ammonia water (*b*)	N/50
	Yellow	$(NH_4)_2Cr_2O_7$	0·42		
	Blue	$CuSO_4.5H_2O$	2·496		
"Cro-Manganate"	Purple	$KMnO_4$	0·0313	(*b*)	N/1000
	Yellow	$K_2Cr_2O_7$	0·487	(*b*)	N/100

(*a*) Made by adding 25 cc. concentrated hydrochloric acid to 975 cc. water.
(*b*) Standard U.S.P. solutions are diluted as required.

TABLE II.—*Matches Obtained with Standard Colours.*

Solutions matched.	Blend used for matching.
Standard Caramel (1 grm. sugar heated to 180° C., then diluted to 500° cc. with water)	"Co-Fe-Cu, 4 -7 -1."
Nessler Test (ammonia dilution equivalent to 1 : 500,000)	"Co-Fe-Cu, 3 9 -0, 50 per cent."
Phenol-Sulphonic Acid Test (1 : 500,000)	"Co-Fe-Cu, 0—12—0, 66 per cent."
Molybdate Assay for Phosphoric Acid (1 : 20,0000)	"Co-Cro-Cu, 0—12 0, 15 per cent."
Folin's Vanillin Test (1 : 100,000)	"Co-Cro-Cu, 3—3—10."
Riegler's Uric Acid Test (1 : 40,000)..	"Co-Cro-Cu, 2—2—8."
Salicylic Acid (1 : 50,000) + proper amount $FeCl_3$ solution)	"Co-Cro-Cu, 7—1—5, 65 per cent."
Naphthylamine Methylamine Sulphanilic Acid Test for Nitrites (1 : 10,000,000)	"Cro-Manganate, 15—1, 55 per cent."

TABLE III.—*Condition and Lovibond Readings of Tests of Ammonium Chloride Using Differently Prepared Solutions of Nessler's Reagent.*

Proportional part of N : Nessler solution used.	Tests with various Nessler reagents.		
	1 to 100,000.	1 to 200,000.	1 to 500,000.
U.S.P. Old (one year old)	Fairly clear	Clear	Clear
U.S.P. Stock (six months old)	Precipitate	Clear	Clear
F. and M. Fresh	Not clear	Clear	Clear
A.P.H.A. Fresh	Precipitate	Clear	Clear
Mason Fresh	Precipitate	Precipitate	Precipitate
Bailey Fresh	Precipitate	Precipitate	Precipitate

Lovibond readings with various Nessler reagents.

1 to 200,000.			1 to 500,000.		
Red.	Yellow.	Blue.	Red.	Yellow.	Blue.
1·9 + 0·2	5·0 + 1·6	−0·2	1·0 + 0·1	3·0 + 0·1	−0·2
1·0 + 1·6	5·0 + 1·9 + 1·0	−0·5	1·0 + 0·1	1·8 + 1·0	−0·1
2·0 + 0·2	5·0 + 2·0 + 1·3	−0·8	1·0 + 0·1	3·0 + 0·1	−0·1
2·0 + 0·7	5·0 + 3·0 + 0·2	−0·3	1·3 + 0·1	3·0 + 0·4	−0·1

possible, since freshly prepared solutions produce an entirely different colour value from that obtained with an aged sample made from the some recipe. As far as we can see, no matter what recipe is followed the older the solution the less likelihood there is of its causing precipitation. The only freshly prepared solution that has been at all satisfactory is that prepared according to the recipe of Frerichs and Mannheim, and in our judgment this recipe should be chosen as the official one for all Nessler tests. Although an old Nessler solution should be used when possible, this is sometimes out of the question, and we recommend the Frerichs and Mannheim modification as the best, since it can be used immediately. This recipe is as follows:—Potassium iodide, 2·5 grms.; mercuric iodide, 3·5 grms.; 15 per cent solution of KOH, 100 grms. Dissolve the potassium iodide in 3·0 grms. of water, add the mercuric iodide, and when dissolved add the solution of potassium hydroxide; let stand until perfectly clear and decant. If needed at once, filter through sand.

TABLE IV.—*Lovibond Readings on Ammonium Chloride Solutions.*

Salt used in solution.	Nitrogen 1 : 250,000.		
	Red.	Yellow.	Blue.
Kahlbaum ..	1·9	4·0 + 2·0 + 0·1	−0·2
Stock	1·9	4·0 + 2·0 + 0·2	−0·2
Old Standard solution ..	2·0 + 0·1	5·0 + 1·6	−0·3

The next problem was to see if a definite reagent, applied in exactly the same manner to solutions of different samples of ammonium chloride, all of the same strength, would give the same colour value. We prepared standard solutions from Kahlbaum's reagent, from stock salt, and from a concentrated standard solution that had been on the shelf for over six months. As shown in Table IV., the results were practically the same in every trial. Only very slight differences were shown by the Lovibond readings, while when compared by the eye no difference at all could be discerned.

It is well known that the tints produced by the action of Nessler's reagent on a solution of ammonium chloride are far from permanent. A solution treated with a freshly prepared sample will show precipitation on standing much sooner than will a solution of the same strength treated with an aged Nessler. With but one exception, the tests made with the various freshly prepared reagents were too unstable in tint to make a second Lovibond reading of any value. The exception was the reagent prepared by the Frerichs and Mannheim recipe, and with this sample readings were made an hour after mixing. The blends were then kept in rubber-stoppered bottles and were read again the next day, with the following results:—

Nitrogen content	Reading.	Red.	Yellow.	Blue.
1 : 500,000	1st	1·0 + 0·1	3·0 + 0·1	− 0·1
	2nd	1·0 + 0·2	3·0 + 0·2	− 0·2
1 : 1,000,000	1st	0·7	1·6	None
	2nd	0·7	2·0 + 0·2 + 0·1	—0·2

For some reason, at present unknown to us, and which will require further investigation, the stronger solution (N = 1 : 500,000) was the more stable.

We next made comparative readings of five tests, each treated with the Nessler reagent "U.S.P. Old Solution," and representing a nitrogen content of 1 : 500,000. The first readings were made within an hour or two after mixing. The tests were kept in rubber-stoppered bottles and read again the following day:—

About One Hour After Mixing.

Solution No.	Red.	Yellow.	Blue.
1.	1·0	2·0 + 0·2	−0·1
2.	1·0 + 0·1	2·0 + 0·4 + 0·1	−0·1
3.	1·0 + 0·2	1·0 + 1·5	−0·1
4.	1·0 + 0·1	1·0 + 1·8	−0·1
5.	1·0 + 0·1	1·0 + 1·5	−0·1
One Day After Mixing.			
1.	1·0 + 0·1	1·0 + 1·5	−0·1
2.	1·0 + 0·1	1·0 + 1·5	−0·1
3.	1·0 + 0·1	1·0 + 1·6	−0·1
4.	1·0 + 0·1	1·0 + 1·5	−0·1
5.	1·0 + 0·1	1·0 + 1·6	−0·1

While these five comparative readings show such slight changes in tint in the course of several hours that the colour can be said to remain almost stable during the time between the two readings, still it is never safe to Nesslerise and then await one's convenience before making colour comparison. We cannot lay too much stress on the fact that in this kind of work it is as necessary to have an exact standard method of procedure as it is to have a standard of colour.

We next tried the tests with a larger amount of the reagent, but results were not satisfactory. We prepared 40 cc. of an ammonium solution and added 10 cc. of Nessler's (Frerichs and Mannheim) reagent, so that in the total volume of 50 cc. the proportion of nitrogen was 1 in 500,000. Another test was made in the same way with the nitrogen content 1 in 1,000,000. In both cases the liquid was a little cloudy, but we managed to get the following Lovibond readings of them, though the colours did not last long and had to be read quickly:—

Nitrogen content.	Red.	Yellow.	Blue.
1 : 500,000	2·0	5·0 + 2·0 + 0·3	−0·1
1 : 1,000,000	0·7	1·5 + 0·7 + 0·2	−0·1

In the paper in the *Druggists' Circular* for March, 1914, there is given a colour match with our standard fluids for Nessler's test, where nitrogen equals 1 part in 100,000, which is "Co-Fe-Cu, 5—7—0." This means that the colour produced by this Nessler test was of the same shade and intensity as resulted when the "Co-Fe-Cu" standard N/2 acidulated coloured solutions were blended in the proportion of 5 cc. of the cobalt solution, 7 cc. of the iron solution, and none of the copper solution.

Recently we repeated colour matches for the Nessler test of nitrogen 1 : 200,000 and 1 : 500,000 with our "Co-Fe-Cu" standard fluids. We made these tests with the "U.S.P. Old" Nessler reagent, and found that the colour of the solution containing 1 part of nitrogen to 200,000 matched our blend of "Co-Fe-Cu, 4—8—0, 70 per cent," while the one having a nitrogen content of 1 : 500,000 matched our blend of "Co-Fe-Cu, 3—9—0, 50 per cent."

This means that to match the tint produced in the Nessler test where nitrogen is present in a proportion of 1 to 200,000 it was necessary to first obtain the best match in *colour quality*, which we found to be a blend consisting of 4 cc. of N/2 acidulated cobalt solution, 8 cc. of N/2 acidulated iron solution and none of the copper solution. The colour *intensity* of this blend was too great to match the Nessler test, so we finally obtained a perfect match by diluting the original N/2 "Co-Fe-Cu, 4—8—0" blend with water to 70 per cent. In other words, we took 14 cc. of the N/2 "Co-Fe-Cu, 4—8—0" blend and added 6 cc. of water, making a total of 20 cc. of coloured fluid. In the same way we matched the Nessler test with a nitrogen content of 1 : 500,000, and found it to be "Co-Fe-Cu, 3 9—0, 50 per cent"—that is, the N/2 blend "Co-Fe-Cu, 3—9—0" was prepared, and then 10 cc. of it was mixed with 10 cc. of water. The Lovibond readings of these two matches were:—

"Co-Fe-Cu."	Red.	Yellow.	Blue.
4—8—0, 70 p.c.	1·9 + 0·2	5·0 + 1·3	−0·3
3—9—0, 50 p.c.	1·0 + 0·1	1·5 + 1·0	−0·2

If these readings are compared with those of the corresponding Nessler tests ("Co-Fe-Cu, 4—8—0, 70 per cent" with N = 1 : 200,000, and "Co-Fe-Cu, 3—9-0, 50 per cent" with N = 1 : 500,000, it will be seen that they are very good matches by the Lovibond method as well as by the eye.

While prosecuting this line of work we investigated the system of standard colour matches for Nessler reactions as laid down in the "Standard Methods of Water Analysis," American Public Health Association, 1913, which consists of two empiric solutions made up as follows:—*Red.*—12 grms. of cobalt chloride dissolved in distilled water; add 100 cc. strong hydrochloric acid and make up to one litre with water. *Yellow.*—2 grms. potassium platinic chloride dissolved in water; add 100 cc. strong hydrochloric acid and make up to one litre with water. These two solutions are blended and diluted in varying proportions, each finished sample being of a tint which is supposed to represent the colour shade and intensity of a certain corresponding Nessler test. We tested this, following the directions in every respect with the utmost care, but we could get no satisfactory results whatever. It is only fair to state that in the book where this method is given no claim is made for its accuracy.

(To be continued).

THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

(Sixth Communication).*

By LEROY McMASTER and A. C. MAGILL.

(Concluded from p. 227).

The Substituted Succinic Acids.

Ammonium Monobromosuccinate.—Mayer and Jacobson state, in their *Lehrbuch der Organischen Chemie*, that when monobromosuccinic acid is treated with a methyl alcohol solution of ammonia the β-monoamide of malic acid results. The exact conditions are not given. No mention is made of the neutral ammonium salt.

When an ether solution of the acid was treated with dry ammonia a fibrous precipitate formed, which soon changed to an amorphous powder. When an alcoholic solution of the acid was used a crystalline precipitate formed. The salt was found to be not deliquescent, and stable in moist as well as in dry air. The salt did not decompose when heated to 50°, but at 100° there was a slight decomposition.

The salt is very soluble in water and acetic acid. The aqueous solution remained neutral for several days. The salt is slightly seluble in ethyl alcohol and much less so in methyl alcohol. It is also very sparingly soluble in ethyl acetate and chloroform, and insoluble in ether, acetone, and benzene. An aqueous solution of the salt gave with silver nitrate solution a white precipitate, insoluble in dilute nitric acid. With ferric chloride solution a yellowish brown precipitate formed, but with lead acetate solution no precipitate was formed.

Calc. for $C_2H_3Br(CO_2NH_4)_2$:—12·12 per cent N. Found:—12·12 per cent (ether); 12·10 per cent (ethyl alcohol).

Ammonium Dibromosuccinate.—Kekulé (*Ann. Spl.*, 1862, i., 354) prepared ammonium dibromosuccinate from an aqueous solution of the acid and found that it crystallised out of water without water of crystallisation.

When ammonia was passed into an ethyl alcohol solution of the acid the neutral salt formed as a fine white granular precipitate. In an ether solution the salt first formed as a gelatinous mass, which changed to a crystalline powder. The salt is not hygroscopic. A solution of the salt in water is neutral at first but becomes slowly acid on standing. The aqueous solution gave with silver nitrate solution a white precipitate, soluble in dilute nitric acid. It also gave a yellowish brown precipitate with ferric chloride solution.

The salt is somewhat soluble in methyl alcohol. It is less soluble in ethyl alcohol than in methyl alcohol. It is soluble in acetic acid and insoluble in ether, chloroform, ethyl acetate, acetone, and benzene. The salt is stable in dry air but loses ammonia in moist air. It decomposes slowly with the evolution of ammonia at 50°. At 100° there is a rapid decomposition.

Calc. for $C_2H_2Br_2(CO_2NH_4)_2$:—9·03 per cent N. Found:—9·00 per cent (ether).

Comparison of Results.—Ammonium succinate has been described by McMaster. The neutral ammonium salts of succinic acid and its substituted bromo derivatives can be prepared in an ether or ethyl alchohol solution of the acids. In ether the salts separate in an amorphous condition and in ethyl alcohol in a crystalline form. All of them are easily soluble in water The aqueous solution of the ammonium dibromosuccinate hydrolyses very slowly. All of the salts described are only slightly soluble in ethyl alcohol. The salts of the bromo derivatives are insoluble in acetone, ether, and benzene. All three salts are stable in dry air, and none of them deliquesce.

Suberic Acid.

Ammonium Suberate.—Gantter and Hell (*Ber.*, 1880, xiii., 1166) prepared the neutral ammonium salt of suberic acid by evaporating an ammoniacal solution of the acid in an atmosphere of ammonia and over potassium hydroxide. They obtained the salt in well-defined leaflets, which completely decomposed at 110° into ammonia and the acid.

The salt could not be prepared in ether on account of the insolubility of the acid in that medium. When dry ammonia was passed into an ethyl alcohol solution of the acid no precipitate formed. Ether was then added to this alcoholic ammonia solution of the acid, whereupon fine white crystals of neutral ammonium suberate formed. A white crystalline precipitate of the salt also formed immediately when the ammonia was passed into an ethyl acetate solution of the acid.

The salt is soluble in water and methyl alcohol, slightly soluble in acetic acid, ethyl alcohol, and benzene, and insoluble in acetone, chloroform, and ethyl acetate. The aqueous solution of the salt does not hydrolyse.

The salt is not hygroscopic. At ordinary temperatures it does not lose ammonia in dry or moist air. At 50° it loses ammonia slowly and at 100° the decomposition is very rapid. At 100° all the ammonia has been liberated and analysis shows that only the acid remains.

Calc. for $C_6H_{12}(CO_2NH_4)_2$: — 13·46 per cent N. Found:— 13·40 per cent (ether alcohol mixture); 13·46 per cent (ethyl acetate); 13·44 per cent (benzene).

Comparison of the Ammonium Salts of the Saturated Dibasic Acids.—We have described in this and previous papers the preparation and properties of the neutral ammonium salts of sixteen saturated dibasic acids, or substituted derivatives of them, not including the hydroxy derivatives. While there is a rather wide variation in their general properties they have many points of similarity. All of them can be prepared in ether, and in every case they separate as amorphous compounds. With the exception of ammonium pimelate all of them readily precipitate in a crystalline condition from an alcoholic solution of the acid. In those salts having both carboxyl groups attached to the same carbon atom there appears to be a strong tendency to deliquesce. With the exception of the pimelate, those salts which have the carboxyl groups attached to different carbon atoms do not deliquesce. The aqueous solutions of the salts of the dibasic acids either do not hydrolyse at all or hydrolyse only very slowly. None of them give off ammonia in dry air except the pimelate. Some of them give off ammonia very slowly in most air. Unlike the salts of the saturated monobasic acids, all of them except the pimelate are only very slightly soluble in ethyl alcohol. The ammonium pimelate thus has different properties in general from the other saturated dibasic acids.

Chlorofumaric Acid.

Ammonium Chlorofumarate.—Perkins (*Journ. Chem. Soc.*, 1888, liii., 699) prepared this salt by allowing the acid to stand in an atmosphere of ammonia. He states that combination takes place with energy, and that if an excess of ammonia be left with the salt there is no decomposition with removal of the chlorine. Perkins also states that on slowly evaporating an aqueous solution of the salt beautiful transparent crystals of the salt separate, which are moderately soluble in water and can be dried at 100° without decomposition. Mushman found these crystals to be monoclinic.

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* For previous papers on this subject see Chem. News, 1913, cviii., 136; 1913, cviii., 182, 193; 1914, cx., 212; 1914, cx., 224; 1915, cxii., 187. From the *Journal of the American Chemical Society* xxxviii., No. 9.

By our method this salt was prepared in an ether solution of the acid. On first passing in the ammonia a colloidal precipitate formed, which passed to a gelatinous mass and then finally to a fine white powder. In a saturated alcoholic solution of the acid a fine flaky crystalline precipitate formed at once. In each case the neutral salt was formed. It is not deliquescent, and gives off ammonia very slowly in moist air. It is readily soluble in water, yielding a neutral solution which does not hydrolyse.

The salt is also soluble in acetic acid. It is very slightly soluble in methyl and ethyl alcohols and insoluble in acetone, chloroform, ether, ethyl acetate, and benzene. It can be heated to 100° without decomposition.

Calc. for $C_2HCl(CO_2NH_4)_2$:—15·17 per cent N. Found:—15·14 per cent (ether); 15·12 per cent ethyl alcohol).

This salt has properties similar to ammonium fumarate, previously prepared in the Chemical Laboratory of Washington University. Both salts readily precipitate from ethyl alcohol, the fumarate as an amorphous powder and the chlorofumarate as fine crystals. Both salts are very slightly soluble in ethyl alcohol, and neither salt deliquesces. Both salts are soluble in water, forming neutral solutions, which do not hydrolyse.

This investigation is being continued with other organic acids and their substituted derivatives.

THE USE OF URANIUM IN ANALYSIS.

By J. C. THOMLINSON, B.Sc.

In the use of uranium solutions for volumetric analysis it is a factor in commercial analysis of constant occurrence that the indicator potassium ferrocyanide is almost useless unless constant care is used in checking gravimetrically.

A standard solution of uranium acetate was made, 1 cc. = 0·0048 grm. P_2O_5, and checked against a solution of $Ca_2P_2O_8$ containing 1 cc. = 0·01 grm. $Ca_2P_2O_8$.

Gravimetrically two experiments gave the calcium phosphate solution.

I. .. .. 1 cc. = 0·011 grm. $Ca_2P_2O_8$
II. .. .. 1 cc. = 0·012 grm. $Ca_2P_2O_8$

Twenty cc. of this solution took 18·1 cc. uranium solution.

Using potassium ferrocyanide, either freshly made or partially oxidised by keeping, does not alter its unreliability unless the greatest care is taken in its use, and either the results are checked as above or the approximate assay content of P_2O_5 is known.

15, Denmark Street, Gateshead-on-Tyne.

ESTIMATION OF MANGANESE IN STEEL.

By J. A. CASHMORE.

Weigh out accurately 1 or 2 grms. of the sample into a 28-oz. beaker. Add about 25 cc. HCl, and heat until dissolved.

When dissolution is complete add a few crystals of potassium chlorate, and evaporate till the free chlorine is driven off. Wash the solution into a 1200 cc. flask, dilute to about 400 cc., and again heat to boiling.

Zinc oxide emulsion is then added in excess (that is, until some of the zinc oxide is seen remaining white in the flask) to precipitate all the iron. Boil for about two minutes.

Filter through a 28 cm. thick filter-paper, and well wash the precipitate with hot water. (A white precipitate of zinc hydroxide may come down in the filtrate, but no notice should be taken of this as it is soluble in excess ammonium hydrate).

Heat the filtrate to about 60° C. Add about a grm. of ammonium persulphate to ensure the oxidation of the manganese. Ammonium hydrate is then added in excess until all the $Zn(HO)_2$ formed is thrown into solution again, and precipitation of the hydrated manganese peroxide is complete. Boil for a few minutes. Filter through a 12·5 cm. Swedish filter-paper, and wash two or three times with strong NH_4OH to remove all traces of zinc salts. Then wash well with hot water. Dry the precipitate, and burn in a hot muffle. Weigh the precipitate, and calculate the percentage of manganese from the weight of the Mn_3O_4, which contains 72·052 per cent Mn.

For strict accuracy it is advisable to dissolve the Mn_3O_4 in HCl, add a few cc. of HNO_3, and reprecipitate the manganese with ammonium persulphate and ammonia. It will be seen that this method abolishes the delicacy of precipitating the iron by neutralising with ammonia, the method most commonly used in laboratories.

11, Neachell Lane, Wednesfield, Staffs.,
October 23, 1916.

ON THE DIGESTIBILITY OF BREAD.*

I. Salivary Digestion in Vitro.

By J. C. BLAKE.

Summary.

The rate of digestion *in vitro* of the starch of bread can be followed readily and accurately by means of the polariscope, the only optically active substance entering the solution under the conditions herein stated being maltose. A rather large array of subsidiary findings surrounds this main observation, such as confirmation of the specificity of the starch of different plants, a clearer identification of some of the ingredients of the starch of the common cereals and the products of their hydrolyses (including two new substances), the variation of the activity of salivary amylase with the dilution and with the temperature, a comparison of amylases of different origin, and a comparison of the salivary digestibility of a number of standard breads. This paper is a report of progress rather than a finality.

Historical.

The statements of Maquenne and Roux (*Ann. Chim. Phys.*, [8], ix., 179; Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1913, p. 1032; Hammarsten-Hedin (Mandel), "A Text-book of Physiological Chemistry," 1914, p. 229), that in the digestion of amylose no considerable amounts of dextrins enter the solution, but that the dextrins ordinarily observed are derived from the amylopectin of starch are greatly at variance with the older ideas of Musculus and Gruber (*Zeit. Phys. Chem.*, 1878, ii., 177), and of Brown and Heron (*Liebig's Ann.*, 1880, cxcix., 65), still current in American works on physiological chemistry (Hawk, "Practical Physiological Chemistry," 1913, p. 61; Mathews, "Physiological Chemistry," 1915, p. 328), according to which boiled starch is a homogeneous substance (Reichart, "Differentiation and Specificity of Starches in relation to Genera, Species," &c., *Pub. Carnegie Inst. Wash.*, 1913, p. 160), which gradually hydrolyses by the continual splitting off of maltose or isomaltose, the residual nucleus passing successively through the stages of soluble starch, amylodextrin, erythrodextrin, and an indefinite number of achroödextrins. So confusing is the literature of this subject, much of which is paraphrased in the works cited, that at the present time none of these ingredients has any standing as a pure chemical substance. On this account the polysaccharides recognised in this work are here defined anew, in close agreement with the general trend of past usage, the word dextrin in particular being applied only to substances markedly diffusible through membranes. The true process of salivary digestion seems to lie about half way between the two processes previously referred to.

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* *Journal of the American Chemical Society*, xxxviii., No. 6.

Experimental.

Polysaccharides.—By working with the starch of bread, as well as with raw and boiled starch, the author was able to recognise more clearly a considerable number of polysaccharides which seem to be chemical individuals, although exhaustive study of each of them is yet to be made. It seems necessary and worth while to record these preliminary observations both for their own sakes and because they were used in indicating *pro tanto* by negation that only maltose was present in the solutions hereafter described.

Cellulose and Amylocellulose.—It should be emphasised that in bread pulp (the white interior of the loaf) the starch granules are not disrupted (Jago, "The Technology of Bread-making," 1911), and that very little of any soluble carbohydrate is present outside the granules, even though the starch is apparently as digestible as boiled starch; whereas in boiled starch the granules are disrupted, and, on long boiling (several hours) or by superheating, go completely into solution. Hence the digestion of the cell walls is the more readily observable with starch from bread, making clear the differentiation of the substance composing the walls from the substances found within the granules. This substance we will call amylocellulose, because of its slow digestibility, the cell walls of the large granules of starch from bread becoming disrupted under ordinary conditions of salivary digestion *in vitro* only after more than twenty-four hours. After forty-eight hours the process is ended, except for a few chain-like cell fragments and the cell-walls of a few very large hexagonal-shaped cells. This definition is at variance with that of Maquenne, who apparently confuses amylocellulose, amylose (the main constituent of cooked starch), and "reverted amylose" (the insoluble and indigestible substance which settles out of starch solutions on standing). Amylocellulose gives no colour with iodine water, as may readily be determined by testing after the cell contents have been removed by digestion (*infra*). It probably hydrolyses through the stage of maltose, and constitutes about 10 per cent of the starch granules (dried at 120°), as indicated by the increase in the polarisation of the digestion mixture after the contents of the cells have been digested (that is, after four hours, Tables I. and IV.). The chain-like fragments and the walls of the hexagonal cells are probably cellulose. The interior of these latter cells stains yellow with iodine, indicating the presence of *protein* (confirmed by digestion with pepsin). All of these features were later recognised in slightly boiled corn and rice starch, indicating great similarity between freshly boiled starch and that of bread, and also that the indigestible cells were not derived from the yeast of the bread.

Amylopectin and Rose-amylose.—If raw cereal starch be treated with iodine water in minimal amount a red colour is developed. This colour disappears at approximately 46°, and reappears at the same temperature provided sufficient iodine was originally added to turn the raw starch purple. The blue tint of the purple disappears during the heating owing to loss of iodine from the solution. The substance giving this red colour with iodine is rose-amylose, first recognised by Day ("Digestibility of Starch of Different Sorts as Affected by Cooking," *Univ. of Chicago Press*, 1908, 37, 41; Reichert, *loc. cit.*, p. 195). It is the substance responsible for most of the confusion existing with regard to the chemistry of starch, since it is usually mistaken for erythrodextrin (Hawk, *loc. cit.*, pp. 10, 65; Mathews, *loc. cit.*, p. 899), and has also been mistaken for "*residual dextrin*," as it is much less readily digested than the dextrins (*infra*). It disappears from ordinary digestion mixtures only after four hours. It is further sharply differentiated from erythrodextrin (*q. v.*) by the difference of 13° in the transition temperature of these two iodides, by the much greater stability of its iodide towards alkalis and toward maltose. The iodide of rose-amylose disappears when the calculated alkalinity (using $NaOH$, Na_2CO_3, or NH_4OH) reaches 0·1 N, whereas the iodide of erythrodextrin disappears when the alkalinity reaches 0·005 N. The difference in the stability of these two iodides to maltose probably accounts for the order of appearance of these iodides, and the common blue iodides of starch on the gradual addition of iodine-water to mixtures of these substances. The iodide of rose-amylose appears first, then the ordinary blue iodides, then that of erythrodextrin. There is no rose-amylose in potato starch.

Rose-amylose is probably a product of the hydrolysis of amylopectin, the substance which gives a freshly-boiled cereal starch solution its excessive viscosity when cool. Addition of saliva to such a viscous solution, or paste, which previously gave a blue colour with minimal amounts of iodine-water, completely destroys the excessive viscosity within half a minute, making the mixture rich in rose-amylose. Arsenic acid of 0·05 per cent or greater concentration (as As_2O_5) completely stops this change of amylopectin into rose-amylose; whereas the same acid at 0·005 per cent lessens the time required for the disappearance of rose-amylose by more than one-half. Santesson found this identical phenomenon in the activity of the catalytic enzyme of frog muscle (*Skand. Arch. Physiol.*, xxxii., 405; *Chem. Abs.*, ix., 2097). Dilute solutions of acetic, butyric, and lactic acids facilitate this change but slightly, agreeing with the results recorded later on that the slight variation in the acidity of different samples of bread does not appreciably affect their rate of digestion. No concentration of these acids was found which completely prevents the change of amylopectin to rose-amylose. Hence, 0·07 per cent arsenic acid was used to stop all digestion, no other change seeming to take place as readily as this, or to take place at all in solutions containing this concentration of arsenic acid. The fate of rose-amylose is being investigated. It probably finally reaches maltose for the most part. The observation of Tanret that the amylopectin contains all the phosphorus found in starch should be noted in this connection (*Bull. Soc. Chim.*, 1915, xvii., 83). A rough estimate of the amount of amylopectin in wheat starch can be made from the polarisations hereafter recorded showing about 10 per cent of amyocellulose, 70 per cent of amylose, and (by difference) 20 per cent of amylopectin. This is in fair agreement with the estimate of Maquenne and Roux, who place the "amylose" which we have seen includes amylocellulose) at 80 to 85 per cent, the amylopectin at 15 to 20 per cent.

Achroödextrin.—If bread or boiled starch digestion mixtures be filtered before the addition of iodine, the rose-amylose may readily be detected in the residue, but the filtrate ordinarily gives no colour with iodine. Hence the theory of Maquenne and Roux, already cited, that no dextrins are present. If, however, alcohol be added to the filtrate during the first few minutes under usual conditions a white precipitate of achroödextrin forms when the alcohol reaches 72 to 80 per cent by volume. Under the conditions of the experiments hereinafter described, a 1 per cent bread suspension gave 0·04 per cent of this dextrin at the end of five minutes, 0·01 per cent at the end of ten minutes, and only a trace at the end of twenty minutes. These values are corrected for a slight precipitate due to the saliva under these conditions. After standing overnight the dextrin was filtered out in a Gooch crucible, dried at 100°, weighed, and redissolved in water. This solution indicated a specific rotation of 170 for this dextrin, a value which is recorded merely to show its properties as a dextrin, the amount worked with being too small to give an accurate result. Further addition of absolute alcohol to the filtrate from this dextrin gave no precipitate or opalescene. Commercial dextrin "precipitated by alcohol" gave 26 per cent of this dextrin.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 2, 1916.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows: –

"*On the Photographic Spectra of Meteorites.*" By Sir WILLIAM CROOKES, O.M., F.R.S.

Thirty rare earthy meteorites, mostly acquired through the courtesy of the British Museum Trustees, have been examined.

The paper first deals with a few novel features in the construction of the spectrograph. The instrument has a train of five double quartz prisms of the Cornu type, and an explanation of their action in preventing double refraction is given. The jaws of the slit are formed of transparent quartz prisms, cut and mounted in such a manner that the edges appear opaque to light. A device, called the ***fixed slit system***, is described by which all uncertainty caused by variation in the width of the slit in various experiments is removed. The aerolites were all examined for occluded gases, with negative results especially for any inert gases that might be present. The spectrum tubes showed only compounds of hydrogen, carbon, and sulphur, and a little free hydrogen. The arc spectrum of each aerolite has been photographed from the region of the ultra-violet to the end of the visible spectrum.

The aerolite was powdered, mixed with powdered silver of known purity, and formed into a cake by hydraulic pressure. This gave sufficient cohesion for manipulation and enables it to conduct the current. The resulting spectrum contained, in addition to the lines of the aerolite constituents, only those due to silver, which are comparatively few. Examples of these spectra are exhibited.

All the lines given in the photographed arc spectra of the thirty aerolites have been identified, and are named in the spectrum atlas. The examination has revealed the presence of unexpectedly large traces of chromium in all the specimens, a condition quite different to that found in the siderites or meteoric irons, where chromium is practically absent.

The proportion between iron and nickel remains constant in twenty-seven out of the thirty aerolites, and is clearly shown in the photographs. In only three nickel is almost absent.

From the experience gained it has been possible to make a mixture containing known quantities of nickel and chromium, which with the addition of iron produces a spectrum in the neighbourhood of the chromium group that is practically identical with that produced by the aerolite ***Aubres***.

"*On Waves in an Elastic Plate.*" By Prof. H. LAMB, F.R.S.

The theory of waves in an infinitely long cylindrical rod was discussed by Pochhammer in 1876. The somewhat simpler problem of two-dimensional waves in a solid bounded by parallel planes was considered by Lord Rayleigh and by the author in 1889. The main object in these investigations was to verify, or to ascertain corrections to, the ordinary theory of the vibrations of *thin* rods or plates, and the wave-length was accordingly assumed to be great in comparison with the thickness.

It occurred to the author some time ago that a further examination of the two-dimensional problem was desirable for more than one reason. The period-equation is, however, at first sight rather intractable, and it is only recently that a method of dealing with it has suggested itself. The result is to give a fairly complete view of the more important modes of vibration, together with indications as to the character of the higher modes which are of less interest.

The paper is illustrated by diagrams of lines of displacement, and by numerical tables.

"*Multiple Integrals.*" By Prof. W. H. YOUNG, F.R.S.

This note gives certain results and formulæ fundamental in the theory of multiple integration with respect to a function $g(x, y, \ldots)$ of bounded variation (integrator). For simplicity, the discussion is confined to two variables. The integrator may, without loss of generality, be taken to be a positive monotonely monotone ascending function, that is, one whose monotone increases with respect to either of the variables has an increasing rate as the other variable increases.

The theory of integration with respect to a monotone function of a single variable, as already developed by the author, may be extended to the present case in view of the following properties of $g(x, y)$. It is continuous, except, possibly, at points lying on a countable set of parallels to the co-ordinate axes, and has an unique limit along each of the four rays parallel to the axes issuing from the point (x, y), as well as in the open quadrants formed by these rays.

Ordinary double integration is integration with respect to the product x, y, and, when absolutely convergent, may always be performed by means of repeated integration. It is striking that in the French language there seems to be as yet no word expressing the distinction between double and repeated integrals. To really grasp this distinction we only have to replace the product x, y by a less special integrator. The calculation of the double integral by repeated integration is then in general impossible. It becomes therefore important to formulate tolerably wide conditions under which such a reduction of difficulty is possible. This is accordingly done in the present communication. Occasion is also taken to obtain other related theorems.

"*Order of Magnitude of the Co-efficients of a Fourier Series.*" By Prof. W. H. YOUNG, F.R.S.

"*A Determination of the Heat of Vaporisation of Water at* 100° *C. and* 1 *Atmosphere Pressure in Terms of the Mean Calorie.*" By T. C. SUTTON.

"*Mechanical Relations of the Energy of Magnetisation.*" By G. H. LIVENS.

The usual mathematical formulation of the relations of the magnetic field leads to the same expression, viz., $\frac{\mu H^2}{8\pi}$ for the density of the energy associated with the field, whether this arises from rigid magnets or from steady currents; but, as in the first case, the energy is treated as potential energy, and, in the second case, as kinetic energy, the apparently consistent result in the two cases really involves a discrepancy.

In the present paper a new formulation of the relations is given which overcomes the difficulty of interpretation in the two cases. The fundamental change made in the work consists in the choice of the magnetic induction vector B, instead of the more usual magnetic force H, to denote the conditions in the æther. This course has long been advocated by Prof. Larmor, but does not appear to have been systematically developed.

It is shown that in the statical case the energy, regarded as potential, can be expressed as the sum of the intrinsic energy of the induced polarisations and a part which appears as though distributed throughout the field with the density $-\frac{B^2}{8\pi}$; and, further, that the same expressions occur in the dynamical case with the proper reversed signs if the energy is treated as kinetic. If the induction follows a linear isotropic law the density of the total energy in the field then appears as $\pm \frac{B^2}{8\pi\mu}$, the positive or negative sign being taken according as the energy is potential or kinetic. In the latter case the present expression for the density is equivalent to the more usual one in parts of the field where there is no rigid magnetism.

INSTITUTE OF ELECTRICAL ENGINEERS.

(Western Local Section, Bristol).

Address of the Chairman, Prof. David Robertson, D.Sc.

Delivered October 23, 1916.

When this Address first began to loom in the distant future, it was my intention to speak a few words to you on the subject of research, but in the interval so much has been written about it that the wind has been taken out of my sails, and little room has been left for anything fresh to be said on my part.

In the past our industries were able to take a leading position in the world, but now our position is neither so good nor so secure as it was. In comparison with our competitors, do we now produce fewer men of genius than formerly, nor does our relatively worse position arise from our making less use of them under the changed conditions?

A century ago the inventive genius, of itself, had a fairly free scope, but in the industrial world of the present day it must be coupled with a much higher degree of scientific knowledge and technical training, and have behind it much greater material resources than formerly if it is to make its influence felt. In the early days of industry the problems to be solved were mainly mechanical, speeds were low, the choice of materials was comparatively small, and the duties put upon them were moderate, while prices were high enough to permit the use of sufficient material to give a good big factor of safety. Only the simplest calculations had to be made, and little scientific knowledge was necessary beyond that acquired in the daily routine of the shops. Consequently, many important advances were made by men having but the slightest theoretical knowledge.

Nowadays, competition requires the utmost to be got out of each ounce of material; higher speeds may cause extra material to be a source of weakness rather than of strength, and introduce phenomena the control of which requires the keenest tools that theory can supply. The advent of electrical transmission has brought into being an entirely new branch of engineering, ever extending its bounds, involving enormously more theoretical knowledge than the older branches, and requiring, in addition, a clearer insight into abstract things. On all hands, calculations must be more exact, and side issues of little importance in the old days have now to be closely taken into account.

The field of knowledge may be likened unto a goldfield. The first comers acquire the surface veins and nuggets with comparative ease and with the crudest equipment; but as these become exhausted their successor must expend more and more preliminary labour without immediate result, and they must possess more and more knowledge if these labours are not to prove altogether fruitless.

In the field of research we are now far past the first stage. The surface treasures which Nature has placed to tempt our further search have mostly been harvested, and the investigator must now be prepared to undergo a long preliminary training before his work is likely to become productive. Consequently, he must have behind him resources sufficiently great to support him during this non-productive period, and to provide the ever-increasing apparatus and materials necessary for carrying on his work.

We have every reason to be proud of the advances made, and being made, by our own countrymen in the domain of science, but at the same time I do not think we put into this work a sufficient number of men of the right sort, of the right training, and of the right temperament. Further, *I do not believe we shall ever get them until we offer them prospects comparable with those open to other professional careers.* It is not sufficient to depend alone on the favoured few whose circumstances enable them to pursue their own ideas without having to worry about the cost or about their bread and butter. To keep up the prosperity of our country we must put the best brains from all classes to those tasks which are most likely to increase the common good.

Let us put ourselves in the position of the father of a boy at school about to determine what his career shall be. If he decides on a classical one and the boy is smart, he can see before him a long vista of highly lucrative posts as an advocate, judge, government official, or administrator in some business or professional capacity. On the other hand, if he considers science he can see little scope beyond a very few well-paid professorships, rather more fairly-paid lectureships, and a host of other teaching posts which besides being underpaid leave but little time for the research work we have in view. A few advanced firms do think it worth while really to pay a scientific worker, but only the fortunate few of those who try to find a market for their scientific knowledge in commercial concerns get much past the stage of a routine tester at a miserable pittance per week. If he is specially lucky he may, for instance, become a charge chemist in a factory under a Government sufficiently enlightened to value his services at just less than those of the labourers whom he directs.

What wonder, then, if the majority of our best youths have their bent directed away from science into what I might call the verbal professions.

I repeat therefore that if our scientific output is to be increased in volume up to our needs and to be maintained at the high level set by our masters of the past, *our first step must be taken at the source by seeing that the scientific career is made sufficiently attractive, in competition with the other professions, to induce a sufficient number of our very best youths to pursue it.*

The scientific side at school must be rescued from the opprobious name of "stinks," and must have equal prestige with the classical. The scientific man must be as greatly respected by the public at large, and must be as highly honoured and as well paid as one belonging to any of the other learned professions. He who sheds new light for our guidance in the future deserves as much kudos from his fellows as one who is full of the precedents of the past, and is certainly more worthy than another whose sole claim to fame arises from his assistance to one of the great political parties in gaining or retaining a parliamentary vote for their own particular shibboleth.

Although legislation can help but little in raising Science to its rightful status, still it can do something. It might, for instance, encourage the study of science in our public schools by insisting on a certain minimum of scientific knowledge in future generations of public officials. It would be unreasonable to ask these to become scientific experts, but a knowledge of scientific thought would enable them to recognise a problem calling for expert assistance, to appreciate the arguments of the expert, and to assist him by suggestions arising from their experience of the conditions surrounding the problem. It would also make them more open to receive new ideas, and so would very materially ease the paths of progress. Even in purely administrative branches such a spirit could scarcely fail to lead to increased efficiency.

Another thing which the Government could do is to make the value and number of the scholarships open to the science boy somewhere about level with those given for classical studies. This could be done either by a special Act diverting part of the present scholarship funds or by the Government themselves founding a sufficient number of new scholarships. Our best schools cannot be dragooned into giving a large place to science against their wish, but they are not altogether insensitive to the claims of the particular examinations which their boys must pass in order to take up their professional career.

By thus making the way to a large number of the lucrative positions lie through a study of science, we should very quickly find every school running a real scientific side, and our universities would then be able to pass away from the condition of having to make their scientific alumni pass their first year in learning elementary work which they ought to have done at school.

We must, however, mainly look to our own men of eminence to bring about a better state of things by continually keeping the needs of science before the proper influential quarters. The war has focussed attention on scientific work with an entirely new force. Never again must public opinion be allowed to forget how much they owe to the often-times obscure worker in the research laboratory. In particular, our leading men must see that their magnificent rally to the assistance of a Government whose "neglect of science" has been their perpetual lament, shall not be misconstrued by the politician and official, and confirm their notion that scientific men are merely theorists whose ideas can usually be neglected, and who are too ætherial to require any encouragement or any visible means of support, but whose assistance can always be obtained, on those rare occasions when it is useful, without any reward, and indeed almost without the trouble of having to ask for it.

In short, our best men must make the Government appreciate the value of their services, and the only way to do that is to see that such services are paid for. Even in these times the "patriotic" politician himself insists on his price before agreeing to some re-arrangement which has become desirable in the national interests, while those who in other lines work for the country "on the basis of pure patriotism" seem to grow wondrous fat in the process. In fact, if we are to judge by the actual payments made by the Government, a single buyer of timber or contractor for army huts is worth far more to the country than several universities of scientific men.

One of the great difficulties in the way of scientific men reaping the due reward of their labours arises from the fact that the benefits of their discoveries are seldom immediately tangible, while at the same time they are open to the whole of mankind. What reward, for instance, did Faraday reap from the discovery of the electric motor and generator; Clerk-Maxwell and Hertz from radio-telegraphy; or Ramsay, Rayleigh, and Dewar from the gas filled lamp? True, none of these things were invented, in a commercial form at least, by these particular men, but their work opened up the new ground which made the inventions possible.

Because of this peculiarity, the highest kind of research work must be supported by mankind at large, which in this country means Parliament and the Exchequer.

The true research worker must possess an infinite patience, a fertile imagination, a wide knowledge of the laws of Nature, and an unbounded faith in the possibility of accomplishing the task on which he is engaged. He must refuse to be diverted from his goal by any reputed impossibility, and if necessary he must be prepared to overthrow accepted ideas when they stand in his way. *The advances of the genius are made by accomplishing the impossibilities of his fellows.* In 1900 Bremer improved the arc light by doing exactly what every one would have said was the wrong thing; before Marconi's experiments in 1901 it was perfectly easy to demonstrate that transatlantic radio-telegraphy must for ever be impossible; in 1910 Coolidge succeeded in drawing tungsten into the finest wires that were ever made in spite of the knowledge among the experts that this metal was far too brittle to be even forged into a rod; in 1913 Langmuir produced the gas-filled lamp when we all knew perfectly well that the best possible vacuum was absolutely necessry for an efficient lamp.

And so it will always be. He is not worthy of the name of pioneer who regards even the laws of gravitation, and of the conservation of energy, mass, and momentum as dogmas which may not be attacked and overthrown when they block his way.

Research is best dealt with in bulk, so that workers in different fields may come into daily intimate contact. A man with a new idea will develop it more rapidly and carry it further if he discusses it over a pipe with a fellow spirit even although the latter can do no more than listen to the exposition. If the subject borders on his own in any way, the cross-fertilisation of the sciences produced by such a discussion may lead to enormous results.

The research worker, however, must also come into close touch with the industrial side of his own subject, without devoting so much time to it that real research gets squeezed out altogether. The man in the factory meets many problems for the solution of which he possesses neither the time nor the knowledge. The scientific man, however willing and competent he may be, would never meet these problems by himself. Keep these two men apart and the problem remains for ever unsolved; but bring their experiences together and progress is sure to follow.

For the success of this co-operation, mutual respect and confidence are required between the manufacturing and scientific sides of industry. This co-operation has been greatly developed with marvellous results in several directions in America, where its realisation has been facilitated by the aggregation of capital into huge trusts. Except in a few of our industries, it is scarcely practical to have that continuous intercourse between the research worker and the factory which is obtained in the well-known American examples, with their real research laboratories attached to, or closely affiliated with, the productive departments. But to some extent the difficulties can be overcome by insisting that the research workers should periodically spend some time in the factory. The duration of these periods must depend on the nature of the work on hand, but they should be as frequent as possible. Even if they amounted to nothing more than a weekly visit to the shops and chats with the managers and foremen, the results would be good, provided that the men in the works did actually discuss their difficulties and give the scientific men the benefit of their own knowledge.

Trade secrets, or supposed trade secrets, stand in the way of that goodwill on the manufacturer's part without which no such scheme can be really useful. But we must either overcome these difficulties, or else we must organise our industries into corporations large enough to bear the expense of huge research departments directed to their own particular ends. Otherwise, we shall in time lose our industries altogether in favour of other countries who may have succeeded in doing one of these things.

Each industry has its own problems which are more or less recognised by those engaged in it. We could all write out lists of what we think we most want in our own sphere; but I wish to direct your attention to one rather big problem of the utmost importance for the future welfare of our own country. I refer to our supply of energy. Past ages have placed vast stores to our credit in the great "Coal Bank," but as we are drawing our cheques upon it with ever-increasing prodigality and nothing is now being paid into it, sooner or later we shall find our cheques returned marked "no funds." It will not occur in our time, but historically speaking the exhaustion of our coal supplies is not remote. It seems fairly certain to come within three centuries, and may even occur within one.

If our country is not to decline into a very inferior position by that time, we must, in the interval, either discover new sources upon which we can draw, or else we must contrive to live within our income.

Our annual consumption of coal is about 200 million tons per annum. Since the energy of one ton of coal is almost exactly one kilowatt-year, we are drawing on our energy capital at the rate of about 200 million kilowatts.

We have, of course, other sources of energy of which we are aware, and possibly many others still unknown. The energy of disintegration of the atoms is enormous; when this is brought under our control we shall have an ample supply for a few ages more, and may even be able to ward off the approach of the next ice age which is due in some thousands of years.

Another large store of energy, mainly derived from the kinetic energy of rotation of the earth, is made available to us through the tides. To raise the level of one square mile of sea by one foot involves the expenditure of about 340 kilowatt-hours. Under ideal conditions of admitting all the water at high tide and releasing it again at low tide, this amount of energy would be available each half tide of, say, 6¼ hours. The tidal power is thus equivalent to about 55 kw. per square mile per (foot rise)^3. Ideal conditions could not be realised, and there would be losses in the turbines, and so we probably err on the high side if we take 10 kw. per square mile per (foot rise)^2 as the maximum we might expect to be able to utilise. This would give 10,000 kw. per square mile with a double tidal amplitude of 31·5 feet, and 500 kw. for one of 7 feet.

The British Channel is by far the most favourable place in this country for the large-scale utilisation of the tides, and I think the Firth of Clyde stands next because of the large area which could be enclosed within a comparatively short dam. We shall not be far out if we take 10,000 kw. per square mile as applicable to the first and 500 kw. to the second of these areas.

A dam across the Bristol Channel from Brean Down to Lavernock Point, taking the Flat Holm on the way, would be under 8 miles in length. It would enclose well over 100 square miles of water, and would give, say, a million kilowatts. One built across below Ilfracombe would be nearly 30 miles long, would enclose quite ten times as much, and might be expected to give us about 10 million kilowatts.

The only possible place for a dam across the Firth of Clyde is the shallow bar somewhere near the Girvan-Kintyre line. It would be in somewhat deeper water than the Bristol Channel ones, would be just over 30 miles long, and would enclose much about the same area as the lower Channel one; but owing to the much smaller tides it would probably give us no more than half a million kilowatts.

I have no doubt that the modern engineer could construct any of these dams within a reasonable time if he were provided with sufficient funds. The capital costs would be very high; I do not know what they would be, but I do not expect that power obtained in that way could compete with our ordinary methods so long as a plentiful supply of coal lasts. Stated in kilowatts they do seem enormous sources of power, but compared with the equivalent of the coal supply which will some day have to be replaced they are quite insignificant. We have, of course, other estuaries which could all be made to contribute their quota, but when all are harnessed I think we shall still be very far short of the equivalent of our present consumption of coal.

With the power available in the electrical form, many economies would be made, but we must remember that our requirements are going up by leaps and bounds, and that these increases would almost certainly exceed the savings from a more efficient use. I therefore think we may conclude that the tides will never do more than replace a quite small part of our coal consumption.

We must now turn our attention to the consideration of our income, which is paid out to us day by day from the sun. The intensity of the sun's radiation as it falls on the earth's atmosphere is somewhere about 5 million kilowatts per square mile of normal surface, which would mean about 3 million kilowatts per square mile of land at our latitude at the equinox noon. Averaging it out throughout the twenty-four hours and throughout the year, we may call it a million kilowatts per square mile here. Over one-half of this, however, is absorbed by the atmosphere, but what is left is ample for our needs and we must find a method of turning it to our own ends before our coal supply is exhausted.

For the economical utilisation of the sun's energy on a large scale it will be necessary to keep the size of the power house within reasonable dimensions, and to provide for keeping it running throughout the twenty-four hours. The direct application of the rays for driving a heat engine, which is quite practical on a small scale in tropical countries, and has actually been done in Meadi in Egypt, would thus scarcely meet our needs even if our climate were suitable, which it is not.

Storage of the energy in some intermediate form is thus necessary to enable us to concentrate it and to level up the discrepancies between the curves of supply and demand.

Nature provides us with such storage in several forms. First, we have gravitational energy in the shape of water raised from the oceans up into the clouds, and this has the especial merit that it makes some use of the areas covered by water. But the smallness of our island makes our share of this bountiful supply somewhat meagre, and consequently we must look to other forms unless some genius will show us how to collect the water high up in the clouds, so that we can utilise the energy now wasted in atmospheric friction by the falling rain. Other countries are more favoured in this respect than ours, and every development of the electrical transmission and utilisation of power increases the advantages which their industries consequently possess over ours.

The winds give another means of temporarily storing the energy received from the sun, partly in the kinetic form and partly in the compression of the air. Here, again, difficulties arise from the uncertainties of the winds, and from the enormous size which a large power windmill would have. Still, research must not dismiss anything as impossible. The rapid advances in the size of steam and water turbines and of electric generators should teach us not to dismiss wind-power as utterly hopeless.

The last form of energy which I shall consider is chemical energy, to which class indeed our coal itself belongs. The only way in which the solar energy is taken up chemically in Nature, so far as I am aware, is through the agency of plant life. *Failing other means, we must grow our fuel.* I therefore offer to our agriculturists the problem of producing a plant having a high calorific value, which shall utilise as high a proportion as possible of the energy falling on the areas devoted to its cultivation, and which shall be suitable for use as fuel, either directly or by distilling alcohol or other spirit from it.

At the same time I ask our electro-chemists to find a method of taking up that energy electrically from the plant, or its products, without first converting it into heat, so as to avoid the large thermo-dynamic losses inherent in the heat engine.

Or better still, I ask our chemists to devise some reaction which will occur with the absorption of energy under the action of sunlight, and which can be reversed, under control, with the return of that energy in the electrical form. *In short, give us a storage battery which is charged by submitting the active materials to sunlight, and which is discharged in the ordinary way.*

As a last resource, in case these should fail, let our ultra-physicists combine with the biologists and produce between them a sufficient number of Maxwell's sorting demons to emancipate us from the second law of thermodynamics.

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for grants must be received by December 8.

NOTICES OF BOOKS.

The Stability of Vulcanised Rubber and the Optimum Cure. The Function of Litharge in the Vulcanisation of Rubber. Part II. *The Influence of the Resinous Constituents.* By Henry P. Stevens, M.A., Ph.D., F.I.C. London: Vacher and Sons, Ltd. 1916. Pp. 23.

The two papers in this pamphlet have been reprinted from the *Journal of the Society of Chemical Industry* for August 31, 1916. In the first of them the author gives a detailed description of his study of the conditions of vulcanisation, and the optimum or perfect cure. He points out that "vulcanisation" proceeds after the actual process is complete, and shows that in determining the optimum cure the question of ageing must be taken into account. In the course of his work he made a very thorough investigation of Eaton and Grantham's optimum cure, and proved that the product was undoubtedly overcured. In the second paper an account is given of the determination of the influence of resinous constituents in vulcanising, and the results show that their removal retards vulcanisation as indicated by the tensile properties and coefficient of vulcanisation.

Technical Chemists' Handbook. By George Lunge, Ph.D. Second Edition, Revised. London: Gurney and Jackson. 1916. Pp. xvi. + 264. Price 10s. 6d. net.

In the second edition of this handbook all the analytical factors have been recalculated on the basis of the atomic weights adopted by the International Committee for 1916, and many other new data are given. As before a careful selection has been made of methods of analysis, and usually only one method is given for each operation, so that uniformity may be established amongst chemists and merchants. The author's wide experience has been invaluable in helping him to decide upon the best method from the point of view of precision and rapidity of execution, and the handbook will be found a very useful laboratory guide for all the common processes employed in analytical chemistry.

Armstrong College. Newcastle-upon-Tyne. Prospectus of Day Classes, Session 1916-1917. London and Newcastle-upon-Tyne: Andrew Reid and Co., Ltd. 1916. Pp. 106.

The buildings of Armstrong College, Newcastle-upon-Tyne, have been in the occupation of the War Office since August, 1914, but the departments of the College have been housed in various different places and the work has been proceeding as far as possible as usual. Certain scholarships are not to be awarded until after the war, but the complete courses of work in science and engineering, &c., are being carried on, and the syllabuses are given in this prospectus, for the guidance of future students, as well as the time tables of the various classes.

The Journal of the Municipal School of Technology, Manchester. Volume VIII. 1914. Pp. 264.

The eighth volume of the journal of the Manchester Municipal School of Technology contains reports of some of the investigations carried out by members of the school during the year 1914. Many of the papers are reprinted by permission from other scientific journals, while in some cases they do not appear to have been published before. They deal with a variety of subjects and show that the school is doing a valuable work in providing a thorough training in the most important branches of scientific industry. The journal has been excellently printed in the Department of Printing and Photographic Technology of the school.

La Chimie des Éléments Radioactifs ("The Chemistry of the Radioactive Elements"). By Frederick Soddy. Translated from the English by E. Philippi. Paris: Gauthier-Villars et Cie. 1916. Pp. iv. + 174. Price 5 fr.

This translation of Prof. Soddy's monograph on the chemistry of the radioelements will be welcomed by French readers as providing them with an authoritative short treatise on a subject which is throwing new light upon many important problems in chemistry. Prof. Soddy's powers of clear exposition are too well known to need emphasising, and his style lends itself admirably to translation into the French language, a task which has been well performed in this book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 13, September 25, 1916.

Acylsemicarbazides.—J. Bougault.—The acylsemicarbazides are usually substances of high melting-point, only very slightly soluble in cold water. The presence of soda or sodium carbonate diminishes the solubility. Warm water dissolves them rather more easily. They are insoluble in benzene, chloroform, petroleum ether, slightly soluble in ether. Alcohol is the best solvent to use for purifying them. When small quantities of hydrochloric acid are added to them chlorhydrates are produced, and may be crystallised from aqueous solution. They are stable salts containing one molecule of HCl to one molecule of acylsemicarbazide. Free alkalis and mineral acids, dilute and boiling, saponify the compounds, giving the free acid and the semicarbazides or their decomposition products—hydrazine, carbon dioxide, and ammonia. Saponification takes place slowly, but oxidising agents attack and destroy the hydrazine group, saponification occurring almost instantaneously. Acetic anhydride does not give an acetyl derivative with the acylsemicarbazides, but simply saponifies them.

Bulletin de la Société Chimique de France.
Vol. xix.-xx., No. 9, 1916.

Researches on Aspirin. Solidification in Concentric Rings of Fused or Dissolved Aspirin.—D. G. Tsakalotos and S. Horsch.—When aspirin is heated on an object glass just to fusion, the melting point not being exceeded, it solidifies not in the usual prismatic crystals but in the form of concentric rings. Usually successive rings are formed round a circular centre, the thickness of the rings gradually increasing from the centre outwards. This method of solidification is so common that it can be employed to identify aspirin. The same result is obtained by the evaporation of dilute solutions of aspirin in ethyl alcohol, acetone, or specially in methyl alcohol, but the centre is usually a prismatic crystal.

Action of Aluminium Chloride on Petrol.—Aimé Pictet and I. Lerczynska.—When aluminium chloride acts on the higher (above 140°) fractions of the distillation of petrol, it converts them partly into light hydrocarbons, among which are representatives of the saturated series C_nH_{2n+2}, and partly into solid unsaturated hydrocarbons which are not volatile without alteration, and which have approximately the composition represented by C_nH_n. The action is not a case of polymerisation and depolymerisation nor of the transport of hydrogen from certain molecules to others, but a much more profound change takes place. Apparently the aluminium chloride first causes the separation of the lateral chains attached to the saturated nuclei of the naphthenes of the petrol. These side chains, taking an atom of hydrogen from the nucleus, form a molecule of a saturated aliphatic hydrocarbon. Thus from the side chain of dodecanaphthene hexane is obtained. From a chemical point of view the residue closely resembles asphalt.

Nitration of Diethylbenzylamine.—E. Nœlting and A. Kregczy.—When dielthylbenzylamine in solution in ten parts of sulphuric acid is nitrated it yields approximately 35 to 40 per cent of the meta derivative, 40 to 45 per cent of the para derivative, and 15 to 20 per cent of the ortho derivative. The three isomers distil under reduced pressure without undergoing decomposition and it would be possible to separate them by fractional distillation, but the separation can be more easily effected by means of the picrates. These derivatives, which can be prepared by adding to the bases the calculated quantity of an alcoholic solution of picric acid, have solubilities in alcohol which bear the relation 1 : 2·4 : 5·83 to one another, and they can thus readily be separated by fractional crystallisation.

Dyes derived from Aminodiethylbenzylamines.—E. Nœlting and A. Kregczy.—When picryl chloride acts on the aminodiethylbenzylamines, products are obtained which possess both acid and basic properties. They can be used to dye cotton mordanted with tannin, the ortho derivative giving an orange yellow coloration and the para derivative a golden yellow. They can also be used to dye silk and wool.

MISCELLANEOUS.

Coal-tar Chemistry and Dye-stuff Research.—The Manchester Municipal School of Technology has recently opened a Coal-tar Chemistry and Dye-stuff Research Department for post graduate study and research. The department will be open to students who have recently graduated, and also to men who have had experience in chemical industry. It aims at forming a central research station for the advancement of knowledge relating to dyestuffs, explosives, and synthetic drugs, and also at preparing students to enter these industries in favourable conditions, after having received a systematic training in the methods of technical research. The proposed course of work is shortly outlined, and the conditions upon which the degrees of M.Sc. Tech. and D.Sc. are to be conferred are stated in a prospectus. The School is to be heartily congratulated upon having undertaken a most valuable work, and the career and output of the new department will be watched with the keenest interest by those engaged in the organic chemical industries.

Institute of Metals.—The 1917 May Lecture will be delivered by Prof. W. E. Dalby, M.A., F.R.S., of the City and Guilds (Engineering) College, who will deal with certain of these methods of testing metals with which his name is so closely associated. Papers intended for the 1917 Spring Meeting should be in the Secretary's hands not later than December 31 next. The following are subjects upon which it is suggested that papers might usefully be contributed:—Boronised Copper; Brass Melting; Die Casting of Metals and Alloys; Effect of Impurities on Commercial Copper with special reference to very small quantities of Zinc; Electric Melting of Copper and Brass; Extruded Brass and Bronze; Extruded Metal; Extrusion Processes; Liquid Fuel in Brass Foundry Practice; Manganese Bronze; Producer Gas in Brass Foundry; Production of Pure Malleable Nickel Sheet; Production of Sound Castings to Stand Hydraulic Test; Rare Earth Metals and their Uses; Standardisation of Bearing of Anti-friction Metals. A ballot for the election of new Members will be held in December. Applications for Membership to be included in the ballot should be received by the Secretary not later than noon on Wednesday, December 13.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Chemical Industry, 8. "Chemistry and Engineering," by Dr. C. Carpenter.

Tuesday, 21st.—Institution of Petroleum Technologists, 8. "The Pyrogenesis of Hydrocarbons," by E. L. Lomax, A. E. Dunstan, and F. B. Thole.

Wednesday, 22nd.—Royal Society of Arts, 4.30. "The Economic Development of Russia and Britain's Share therein," by Leslie Urquhart.

Thursday, 23rd.—Royal Society. "The Scattering of Plane Electric Waves by Spheres," by T. J. I'a Bromwich. "Numerical Results of the Theory of the Diffraction of a Plane Electromagnetic Wave by a Perfectly Conducting Sphere," by J. Proudman, A. T. Doodson, and G. Kennedy.

TO comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged in Government work will be engaged."

As Chief or Assistant. Twelve years' experience—England, U.S.A., Canada, in Steel and Iron Works; at Mines, North Africa, West Indies. Now shift Foreman in Canadian Steel Works Laboratory. Nothing under £4.—Address, S. I., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Wanted, Assistant Chemist for Laboratory Work. Must be ineligible. Write, giving full particulars as to education and experience, together with salary required.—Address, W. A., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

Wanted, Set of BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT in good condition and complete to recent date.—State details and price to W. H. W., Chemical Department, Northern Polytechnic Institute, Holloway, N.

WITTE'S PEPTONE, or Peptone of Equivalent Value.—Supply wanted for use with Rideal-Walker Test.—Reply to "Witte," care of Wilcox and Co., 26, Martins Lane, Cannon Street, E.C

ALFRED JÖRGENSEN
LABORATORY FOR THE PHYSIOLOGY AND TECHNOLOGY OF FERMENTATION.
30, FRYDENDALSVEJ, COPENHAGEN, V., DENMARK.
STUDENTS' SECTION.—For Beginners and Advanced Students with Practical (Brewers, Distillers, &c.) or Scientific purposes in view.
ANALYTICAL AND PURE CULTURE SECTION.—All kinds of Research Work. Pure Cultures: Brewers', Distillers', Air, Vienna, Wine Yeast, &c.; Lactic and Acetic Ferments, Starters (for Dairies, &c.). Methods and Cultures for Manufacture of Beers containing a *Low Percentage* of Alcohol.
New Methods for Distilleries and Factories of *Air*-grown and *Vienna* Yeast, including such as use *Molasses*. Increased yields. Yeast of better keeping properties.
Prospectus and further particulars on application to Director.

THE CHEMICAL NEWS

Vol. CXIV., No. 2974.

COLOUR STANDARDS AND COLORIMETRIC ASSAYS.*

By H. V. ARNY and C H. RING.
College of Pharmacy, Columbia University, New York.

(Continued from p. 237).

Nitrate Determination.

In the work on determination of nitrates we have employed the methods as directed in the "Standard Methods for Examination of Water and Sewage," A.P.H.A., 1913; Mason's "Examination of Water; and other reference books. As is well known, the yellow colour of the nitrate test is as stable as could be desired. After proving this stability sufficiently, three different lots of potassium nitrate—"Kahlbaum reagent," an average sample in crystal form, and still another in powder, that were taken from stock—were submitted to comparative tests. Standard solutions were prepared, according to directions, with phenol-sulphonic acid; *i.e.*, a standard solution was evaporated to dryness, phenol-sulphonic acid added to the residue, and then water added in sufficient amount to make a standard solution that would be of a strength appropriate to our use. When the final standard solutions, or portions thereof diluted, were treated with ammonia water, uniform colour intensity was obtained from solutions of the same strength as Lovibond readings in Table V. show.

Table V.—*Lovibond Readings* (*Yellow only*) *on Potassium Nitrate.*

Salt used in solution.	Nitrogen 1 : 1,000,000.		Nitrogen 1 : 2,000,000.	
	1st reading.	2nd reading	1st reading.	2nd reading.
Kahlbaum .	2·0+0·05	2·0+0·07	1·0+0·04	1·0+0·07
Crystal ..	2·0+0·05	1·9+0·1	1·0+0·05	1·0+0·04
Powder ..	2·0+0·1	2·0+0·1	1·0+0·05	1·0+0·04

The very slight differences shown are much more likely caused by changes in the vision of the person reading than by any change of colour in the liquid. This colour was of such a pure yellow that it was found only necessary to use yellow Lovibond glasses when making the readings. In some of the tests the amounts of phenol-sulphonic acid and of ammonia water employed were varied from the regulation quantities, in order to note the influence of such deviation; variations within reasonable bounds made no difference in the resulting colour, all tests of equal strength of nitrogen producing equal colour values.

We also found that while most authorities direct the use of 100 cc. of volume for each test, 50 cc. of nitrate solution and half the usual quantity of ammonia water gave practically the same colour value as the usual amounts. To facilitate diffusion we used glass-stoppered cylinders in place of Nessler tubes.

In all cases where the matching of coloured fluids was not carried out with the Lovibond tintometer we used 1-oz. Blake bottles, these being filled from the glass cylinders used for making the determinations. Rubber stoppers were used for alkaline solutions and corks for acid mixtures.

In Table VI. are given the Lovibond readings obtained on another line of tests which were kept in Blake bottles. Only the stronger solutions showed any considerable colour change.

Table VI.—*Lovibond Readings, using Blake Bottles.*

Nitrogen content.	Red.	Yellow.	Blue.
Read shortly after mixing.			
1 : 2,000,000	None	1·0+0·05	None
1 : 1,000,000	0·1	2·0+0·1	None
1 : 500,000	None	5·0	None
1 : 250.000	None	5·0+2·0+1·6	None
1 : 200.000	None	5·0+3·0+1·6	None
1 : 150,000	None	5·0+4·0+1·6	−0·1
1 : 125,000	None	5·0+4·0+2·0+0·1	−0·2
Read one or two days after mixing.			
1 : 2,000,000	None	1·0+0·07	None
1 : 1,000,000	None	2·0+0·1	None
1 : 500,000	None	5·0	None
1 : 250,000	None	5·0+2·0+1·5	None
1 : 200,000	None	5·0+3 0+1·6	None
1 : 150,000	None	5·0+4·0+1·8	−0·1
1 : 125,000	None	5·0+4·0+2·0	−0·1
Read three weeks after mixing.			
1 : 2,000,000	None	1·0+0·5	None
1 : 1,000,000	None	1·9+0·2	None
1 : 500,000	None	3·0+1·5	None
1 : 250,000	−0·1	5·0+3·0+0·2	None
1 : 200,000	−0·1	5·0+3·0+0·7	None
1 : 150.000	−0·1	5·0+4·0+2·0	−0·2
1 : 125,000	None	5·0+4·0+1·6	−0·5

In looking for blends of our standard fluids that matched the colour produced by these nitrate tests, we found that N/2 acidulated ferric chloride solution was of exactly the right tint, making blending unnecessary. We merely diluted this with water, according to the strength of the nitrate tint that was to be matched. Only three nitrate tints (nitrogen content 1 : 500,000, 1 : 1,000,000, and 1 : 2,000,000) were thus matched. From several trial dilutions of the N/2 ferric chloride solution we selected three to compare with each nitrate test, making in all nine samples of iron solution. These were placed in 1-oz. Blake bottles, as were the three nitrate tests, and the twelve fluids were matched as "unknowns." The ferric chloride matching fluids were made by diluting the N/2 solutions to the following percentage strengths:—16⅔, 20, 25, 28½, 33⅓, 40, 66⅔, 75, and 80; *i.e.*, 20 per cent fluid was made by diluting 1 part of the N/2 solution with 4 parts of water.

The twelve fluids, each bearing a key number, were then submitted to three observers for matching, and the results were as follows:—Nitrate solution containing 1 N to 2,000,000 was found by all observers to stand between the 25 per cent and 20 per cent N/2 ferric chloride solution, with the 25 per cent as a better match. The 1 N to 1,000,000 was found by all observers to stand between the 40 per cent and the 33⅓ per cent N/2 ferric chloride, without being able to decide which was the better match. The nitrate solution containing 1 N in 500,000 proved more difficult to match, while all observers agreed that the 66⅔ per cent N/2 ferric chloride solution was closest, the other two ferric chloride solutions picked out as nearly matching—75 per cent and 80 per cent of N/2 strength—were so similar in hue to the 66⅔ per cent dilution that the observers could not agree on the proper sequence.

In the order dark to light, Observer A reported 75 per cent, 80 per cent, nitrate solution, 66⅔ per cent; Observer B reported 80 per cent, nitrate solution, 66⅔ per cent, 75 per cent; and Observer C 75 per cent, 80 per cent, 66⅔ per cent, nitrate solution. This confirms the statement made in a previous paper, that the average eye cannot discern, in ordinary cases of matching colour, differences of less than 5 per cent. Lovibond readings were made of all 12 samples, and the results are shown in Table VII.; since all were matchable with the yellow Lovibond glasses alone, the "red" and "blue" columns

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* From *Journal of Industrial and Engineering Chemistry*, viii., No. 4.

Table VIII.—*Comparative Lovibond Readings of Nitrite Solutions.*

Nitrogen.	Reagent.	Red.	Yellow.	Blue.
1 : 1,000,000	A.P.H.A.	5·0+4·0+3·0+2·0+1·0+1·9	−1·9	−1·5
	A.P.H.A. (*a*)	5·0+4·0+3·0+2·0+1·0+1·6	−2·0	−1·3
	Mason	5·0+4·0+3·0+2·0+1·0+1·9	−1·9	−1·5
1 : 2,000.000	A.P.H.A.	5·0+4·0+3·0+0·7	−1·5	−1·0
	A.P.H.A. (*a*)	5·0+4·0+3·0+1·0	−1·5	−0·7
	Mason	5·0+4·0+3·0+1·0	−1·5	−1·0
1 : 5,000,000	A.P.H.A.	4·0+1·6	−0·3	+0·1
	A.P.H.A. (*a*)	5·0+1·6	−0·4	None
	Mason	5·0+1·5	−0·3	+0·1
1 : 10.000,000	A.P.H.A.	3·0+0·4	None	+0·3
	A.P.H.A. (*a*)	4·0	None	+0·3
	Mason	4·0+0·2	−0·1	+0·2
1 : 14,000,000	A.P.H.A.	1·0+1·3	None	+0·2
	A.P.H.A. (*a*)	1·0+1·8	None	+0·2
	Mason	3·0	None	+0·2
1 : 18,000,000	A.P.H.A.	1·9	None	+0·2
	A.P.H.A. (*a*)	2·0+0·1	None	+0·2
	Mason	2·0	None	+0·1
1 : 20,000,000	A.P.H.A.	1·5+0·2	None	+0·2
	A.P.H.A. (*a*)	1·9	None	+0·2
	Mason	1·9	None	+0·1

(*a*) Acidified by the addition of mixture of acetic and hydrochloric acids to the tests.

are omitted. These results prove that the simple bottle readings agree so closely with the Lovibond readings that for practical purposes our N/2 acidulated ferric chloride, properly diluted, can be used as a standard for the quantitative determination of nitrogen as nitrates in minute quantities. Thus if the colour of a nitrate test matches the colour of a N/10 acidulated ferric chloride standard fluid, such a solution contains nitrogen as nitrates in the proportion of 1 : 2,000,000. If the colour of the test matches the colour of the N/6 standard fluid, the proportion of nitrogen will be 1 : 1,000,000.

Table VII.—*Lovibond Readings of Diluted* $FeCl_3$ *Solutions.*

$FeCl_3$.	Yellow.
1 N in 2,000,000 (yellow 1·0+0·05).	
16⅔ per cent	0·7+0·2
20 ,,	1·0+0·1
25 ,,	1·0+0·2
1 N in 1,000,000 (yellow 2·0+0·1).	
28½ per cent	1·5+0·1
33⅓ ,,	1·9+0·1
40 ,,	2·0+0·4
1 N in 500,000 (yellow 5·0).	
66⅔ per cent	3·0+1·3+0·1
75 ,,	5·0+0·1
80 ,,	5·0+0·7

The scope of this plan of assay is limited only by the ability of the eye to discern the yellow tint in the solution. In tests where nitrogen is present in less than 1 : 2,000,000 the tint is too light to read satisfactorily with the Lovibond tintometer, unless a layer of fluid several inches through is employed. In very tenuous solutions it would, of course, be necessary to examine and compare the colour through a considerable layer of fluid, as is done regularly in water analysis by using Nessler tubes; but in these cases dilutions of the standard ferric chloride fluid can be used for comparison in such tubes.

In the foregoing paragraphs we have shown that the nitrate colorimetric test of nitrogen content 1 : 500,000, 1 : 1,000,000, and 1 : 2,000,000 match our standard acidulated ferric chloride solutions of 66⅔ per cent, 40 per cent, and 25 per cent of N/2 strength respectively, and this we believe demonstrates the fact that any other readable nitrate fluid so treated has an exact counterpart in a dilution of our acidulated ferric chloride standard fluid.

Nitrites.

The accepted colorimetric method for the determination of nitrogen in the form of nitrites in an extremely dilute solution of sodium nitrite, with sulphanilic acid and a naphthylamine salt, was then investigated. We found that the colour produced could not be directly matched by any combination of the red, yellow, and blue Lovibond glasses. Of course, the red colour predominated; but when red Lovibond glasses were compared with the solution the tint of the latter was so much more brilliant than the tint of the red glasses, that both yellow and blue glasses had to be placed against the cell containing the fluid in order to obtain a satisfactory match, thus subduing the real colour of the nitrite solution. We were thus able to use the tintometer as a basis of comparison, and thus we also secured perfect colour matches with some of our standard coloured fluids, as will be presently shown.

In this test we used two different sets of reagents. The first, which is sanctioned by the A.P.H.A. book on water methods, was prepared by dissolving each of the two reagents in 5 N acetic acid; 2 cc. of each of the reagents were added to 100 cc. of solution containing the sodium nitrite. The second set, prepared according to "Examination of Water," by W. P. Mason, was made by dissolving the proper amount of sulphanic acid in hot water, and the naphthylamine hydrochloride in boiling water. Two cc. of each of these reagents were added to 100 cc. of solution containing the nitrite which was first acidulated with a drop of concentrated hydrochloric acid.

Comparing the effects of these two sets of reagents, it was found that with hydrochloric acid present a slightly darker tint was usually obtained. We also tried acidulating the solutions with a small amount of a mixture of acetic and hydrochloric acids when using the acetic acid reagents. This produced about the same colour results as were obtained with the hydrochloric acid reagents, and also seemed to effect greater permanency in the tint as is indicated in Table VIII. We found that slight variations in the amounts of reagents used made no perceptible difference in the colour results, also that 50 cc. of the nitrite solution containing about half the quantity of reagents was always of the same colour value as 100 cc. of the same solution containing the regular quantity of reagents. Making Lovibond readings of a few of the stronger nitrite solutions we found that the strongest ones, particularly the one in which the nitrogen content was 1 : 1,000,000, had to be read within fifteen or twenty minutes after mixing, although the ones to which both acetic and hydrochloric acids were added lasted longer than the others.

To study the effect of time on the tint produced, we repeated the experiment, using the acidified A.P.H.A. reagent, which we found the most satisfactory of the three. As solutions representing more than nitrogen 1:300,000,000 were not permanent in colour after two hours, the solutions read had strengths ranging from 1 : 3,000,000 to 1 : 20,000,000. The matching of the colour of the nitrite tests with our standard coloured fluids was not easy, since the colour produced by the addition of naphthylamine and sulphanilic acid reagent to a solution of nitrite is in a class by itself. In very dilute solutions it is a brilliant pink, while in stronger ones it is more like a shade of carmine. Since all of the nitrite tints have suggestions of blue or violet, none of the "Co-Fe-Cu" blends were like them. Fairly close matches were obtained with some of the "Co-Cro-Cu" fluids, and as a preliminary to matching the appropriate blends of the standard N/50 "Co-Cro-Cu" fluids were diluted with water and then submitted to Lovibond readings.

TABLE X.—*Lovibond Readings of* N/50 "Co-Cro-Cu" *Blends.*

Dilution (per cent).	Red.	Yellow.	Blue.
	"Co-Cro-Cu, 10—0—2."		
20	1·5	None	+0·1
25	1·6	None	+0·1
30	1·6	0·2	None
35	1·9	0·1	0·1
40	2 0+0·2	0·1	None
45	2·0+0·3	None	None
50	1·0+1·6+0·1	None	None
60	2·0+1·3+0·1	None	None
70	4·0+0·1	None	0·1
80	5·0+0·4	None	0·2
	"Co-Cro-Cu, 9—0—3."		
20	1·3	None	0·2
25	1·5	None	0·2
30	1·6 +0·1	None	0·2
35	1·9	None	0·2
40	2·0+9·1	None	0·2
50	1·0+1·8	None	0·3
60	3·0+0·4	None	0·4
70	4·0+0·2	None	0·4+0·1
85	3·0+1·8	None	0·7
100	5·0+1·3	None	0·7+0·1

These readings (Table X.) show that the colour of some of the nitrite tests is very closely matched by some of the "Co-Cro Cu" blends. Thus the Lovibond reading for nitrogen 1 : 18.000,000 in Table IX. is exactly the Lovibond reading of blend "Co-Cro-Cu, 9—0—3, 40 per cent" found in Table X. Nitrite tests of other strengths can also be matched as closely as this, as far as Lovibond readings are concerned, but, curiously, these fluids of equal Lovibond values do not necessarily match when compared in Blake bottles. When so compared the colour quality does not appear to be the same, for a peculiar tinge which is characteristic of the nitrite test is lacking in the "Co-Cro-Cu" blends. For practical purposes of analysis, however, these matches would be entirely satisfactory, but for exact work they left something to be desired; we solved this difficulty by means of blends of the potassium permanganate and potassium dichromate standard coloured fluids. These blends are not at all stable, and, as mentioned above, should be prepared freshly when needed. Preliminary to matching the colour of these blends with the tints produced in the nitrite tests we made Lovibond readings of them as soon as possible after mixing, read them again on the following day, and again on the third day.

(To be continued).

ON THE DIGESTIBILITY OF BREAD.[*]

I. SALIVARY DIGESTION IN VITRO.

By J. C. BLAKE.

(Concluded from p. 241).

Maltose was rather sharply identified as follows:—A 1·00 per cent (final concentration) suspension of disintegrated bread (Table II.), which gave a reading of about 0·1 per cent on the polariscope, which read percentages of *d*-glucose, directly gave readings of about 1·0 per cent within a few minutes after mixture with saliva in moderate amount. In the absence of maltase and proteolytic enzymes the readings slowly increased to about 1·30 (Table I.), this slow increase registering for the most part the slow digestion of the rose-amylose and the amylo-cellulose. The initial rapid rise in the polarisation seems to be due to the digestion of the main content of the starch granules (which we may call *amylose*), the optical activity after the digestion of the achroödextrin (first fifteen minutes) being wholly due to maltose. The absence of dextrins is indicated not only by the negative tests with iodine and absolute alcohol, but by the unbroken asymptotic curve (Fig. 1, for Bread No. 1, Table I.).

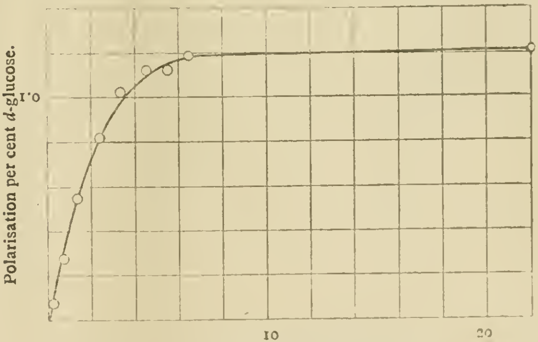

FIG. 1.

The absence of *d*-glucose in appreciable amounts is indicated by negative tests for glucosazone and with a modification of Barfoed's reagent—twice as much copper acetate being used as that ordinarily specified (Hawk, *loc. cit.*, p. 443) and the time of boiling being one-half minute—and also by comparison with results obtained when maltase was present. A further pseudo-quantitative proof that only maltose was present in the solutions referred to is the fact that that on partial hydrolysis with acids they show the same change of optical activity as a solution of pure maltose having the same polarisation. Thus, when such solutions are beated half an hour in boiling water with 3 per cent of concentrated hydrochloric acid (by volume), each loses one-third its optical activity. The difficulty of completely hydrolysing maltose with acids, owing to the reversibility of the reaction, is well

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[*] *Journal of the American Chemical Society*, xxxviii., No. 6.

TABLE I.—*Polarisations Read as* d-*Glucose.*

	Wheat No.									Spoiled yeast.		
Time of fermentation	1. 0·5 norm.	1. norm.	1. 2 norm.	1. Duplicate norm.	2. 0·5 norm.	2. norm.	2. 2 norm.	3. norm.	4. norm.	1. norm.	2. norm.	3. norm.
Time of digestion (hrs.).												
0·25	0·09	0·14	0·17									
0·50	(0·18)*a*	(0·23)*a*	(0·20)*a*	0·24	0·67	0·64	0·68	0·65	0·67	0·19	0·81	0·38
0·75	0·27	0·33	0·37									
1·50	0·55	0·64	0·62	0·72	1·12	1·04	1·05	0·90	1·17	0·63	1·24	0·88
2·50	0·83	0·90	0·88	1·03	1·12	1·15	1·13	1·01	1·19	0·89	1·23	0·97
3·50	1·02	1·07	1·08									
4·50	1·13	1·19	1·12		1·12	1·16	1·14					
5·50	1·13	1·17	1·14									
6·50	1·19	1·15	1·23									
22	1·21	1·21	1·34									
23					1·11	1·13	1·00					
45				1·09				0·96	0·94			
71					0·77	1·01	0·99					
316										0·89	1·00	0·70
Normal acidity..	0·00019	0·00015	0·00026	0·0007	0·00010	0·00010	0·00012	0·00012	0·00012	0·00004	0·00007	0·00012
Original polarisation..	0·08	0·03	0·00	0·02	0·05	0·02	0·04	0·08	0·10	0·09	0·04	0·10
Digest. coefficient (per cent). ..	15	19	22	20	56	53	57	54	56	16	67	32

(*a*) Interpolated.

TABLE II.

				Duplicates.					
Wheat No. :—	1.	1.	1.	1.	1.	1.	2.	2.	2.
Time of fermentation.	½ norm.	norm.	2 norm.	½ norm.	norm.	2 norm.	½ norm.	norm.	2 norm.
Time of digestion (hours).									
0·25	—	—	—	—	—	—	0·91	1·12	0·97
0·50	1·08	1·01	1·17	1·09	1·02	1·13	—	—	—
0·75	—	—	—	—	—	—	1·01	1·16	1·18
1·50	1·05	1·08	1·04	1·09	1·13	1·14	1·05	1·08	1·04
2·50	—	—	—	1·08	1·05 ?	1·09	0·84	1·10	1·10
3·50	1·00	1·00	1·06	1·05	1·14	1·10	0·83	1·05	1·02
4·50	—	—	—	1·00	1·05	1·08	—	—	—
22	0·78	0·89	0·81	—	—	—	0·82	0·99	1·14 ?
23	—	—	—	0·89	0·97	0·94	—	—	—
71	0·79	0·89	0·79	—	—	—	—	—	—

TABLE IV.

				1 p c. commercial ptyalin.			
				Home-baked bread, No. 8.		Commercial bread, No. 9.	
Time of digestion Hrs.	Colour of starch with iodine-water in small amount.	Colour with iodine, due to	1 p c. diastoid. Freshly boiled rice starch.	Moist.	Air-dried.	Moist.	Air-dried.
0·00	Blue	Starch..	0·64				
0·75				0·62		0·68	
1·00	Red → violet	Rose-amylose	2·62		0·25		0·28
1·75				0·96		0·86	
2·00	Pink → light purple	„	2·42		0·67		0·60
2·75				1·06		1·04	
3·00	Light purple	„	2·46		0·99		0·88
3·75				1·14		1·10	
4·00	Colourless		2·42		1·28		1·18
4·75				1·22		1·12	
	Large amount of iodine-water		2·48(*a*)		1·44		1·34
5·00	Purple..	Red-amylose					
6·00	Purple..		2·48				
7·00	Purple..	„	2·50				
24	Trace of purple.. ..	„	2·70				
25	Pink	„	2·60				
26	Pink	„	2·64				

(*a*) Filtrate turbid; efilter.

known (Daish, *Journ. Chem. Soc.*, cv., 2053). Finally, the reading 1·30, read as *d*-glucose, corresponds to 0·47 per cent starch, using the equations—

$$\text{P.c. maltose} = \text{rotation as } d\text{-glucose} \times \frac{52\cdot5}{138\cdot3},$$

and—

$$\text{P.c. starch} = \text{p.c. maltose} \times \frac{324}{342},$$

in close agreement with the percentage of starch usually present in bread – 50 per cent (Jago, *loc. cit.*, p. 540), and that indicated by the usual method of testing. (This bread contained 40·0 per cent water and 8·0 per cent gluten, besides salt and other minor ingredients). Maltose shows little multirotation, and isomaltose from starch if present has the same specific rotation as maltose. In so far as the optical activity is due to maltose, multiplication of the readings recorded in the tables by 0·36 gives the percentage of the original material represenred by the starch digested at the time the reading was made.

On this basis Wheat No. 2, Table II. (average of three samples), at the end of fifteen minutes (the time the achroödextrin disappears from the filtrate) showed a digestion of 72 per cent of the estimated amount (0·50 per cent) of starch present. Although maltase from the disintegrated bread was present in these experiments, as indicated by the subsequent decrease in the polarisations, yet the rate of such decrease is such that it would be negligible for the first fifteen minutes.

The complete or nearly complete change of starch into maltose has been claimed by Maquenne (*loc. cit.*) and by Fernbach and Wolff (*Comptes Rendus*, cxlv., p. 80) and others (Syniewski, *Liebig's Ann.*, cccxxiv., p. 214) as determined by copper reduction, polariscopic, and other methods.

Erythrodextrin was clearly recognised as follows:—Bread was digested in the presence of toluene with saliva diluted with 99 volumes of water. Under these conditions at the end of fifteen minutes 60 per cent of the total amount of starch present was found in the filtrate as erythrodextrin, as determined colorimetrically after the addition of arsenic acid and iodine water. The amount of erythrodextrin in the digestion mixture gradually decreased, disappearing at the end of two hours. The standard erythrodextrin solution for colorimetric comparison was prepared from a white commercial "Dextrin, precipitated by Alcohol," which contained only a trace of insoluble matter and of amylodextrin (*infra*), by precipitating the erythrodextrin with 65 per cent alcohol (final concentration). The erythrodextrin began to precipitate when the concentration of the alcohol reached 50 per cent, but achroödextrin did not begin to precipitate in the filtrate from the erythrodextrin until the concentration of the alcohol reached 72 per cent. These sharp limits of precipitation rather indicate that each of these dextrins is a pure substance. The transition temperature of this iodide is 33°. A 0·5 per cent solution of erythrodextrin is completely digested to the achromic point by 1:7 saliva in two minutes at the ordinary temperature. During the spontaneous fermentation of starch solutions containing no preservative but iodine the starch passes through a stage in which the only colour given with iodine water is the iodide of erythrodextrin. (For other properties, see rose-amylose).

Amylodextrin was clearly recognised and estimated in the filtrate of the slow digestion experiment just described. It gives a pure blue colour with iodine water, which forms before the indide of erythrodextrin does in solutions containing both these substances. The transition temperature of the iodide is about 50°. Estimated in the filtrate by colorimetric comparison (Dermstedt, *Ber.*, xxviii., ref. 1025, among others employed this principle) with wheat starch boiled one hour only 0·007 per cent was present at the end of fifteen minutes, only a trace at the end of forty-five minutes, and none at the end of ninety minutes. Amylodextrin is therefore more readily digestible than erythrodextrin, which it probably hydrolyses into. The three dextrins already mentioned not only diffuse through the cell walls of the starch granules of bread, but also through goldbeaters' skin.

Red-amylose and a new substance, which we will call *Blue-amylose*, require brief mention. Ordinary (unfiltered) digestion mixtures of bread or of boiled starch, in which the amylose and the rose-amylose have been completely digested, as determined by the methods already given (that is to say, after five hours), and in which no erythrodextrin is present, colour a deep red on the addition of iodine water in comparatively large amounts. The transition temperature of this iodide is 73°, but if the solution is heated somewhat above 80° the red colour no longer reappears on cooling the solution through 73°, but a blue coloration begins to appear as the solution is cooled through 83°. The substance giving the red colour under these conditions agrees with Day's description of red-amylose (Day, *loc. cit.*, 37, 41; Reichert, *loc. cit.*, p. 195). It is probably a product of the hydrolysis of amylocellulose and probably hydrolyses into blue-amylose. Blue-amylose is best obtained by boiling the residue of a digestion mixture after it no longer colours pink with small amounts of iodine water—that is, after four hours.

A new dextrin giving with iodine water a blue iodide (whence we may call it *Cyanodextrin*), which forms before the iodide of rose-amylose in mixtures containing both these substances, and the transition temperature of whose iodide is sharply 29·5° (uncorrected), has also been recognised, but as it does not appear in the sequel of this paper it will not be further discussed in this place.

It must be added, in order to avoid the erroneous deduction often met with in the literature (Bayer and Field, *Journ. Chem. Soc.*, 1912, ci., 1403) to the effect that potassium iodide changes the blue iodide of starch to red, that potassium iodide in solutions one-fourth saturated really destroys the blue iodide of starch, but does not affect the iodide of either rose-amylose or erythrodextrin, even when added to saturation. This principle was confirmed by the fact that the amount of erythrodextrin present in a mixture of dextrins and starch could be estimated colorimetrically in the presence of potassium iodide and alcohol (toward which reagent the red iodides are the more stable), even when the amount of starch present was varied within wide limits. Furthermore, solutions of blue iodides containing no erythrodextrin, rose-amylose, or red-amylose do not turn purple or red on the addition of potassium iodide, but pass through green in disappearing.

Conditions of the Digestion.—All the materials used in these experiments were preserved with toluene (except takadiastase, which quickly moulds in solution), and the digestions took place in the presence of toluene. The enzymes used were saliva, commercial ptyalin, Horlick's "diastoid," and takadiastase. The three latter were used in final concentration of 1 per cent, the saliva in final concentration of 1 in 8, except where otherwise stated. The standard breads were prepared from the standard flours listed below, and were baked by standard commercial methods by J. C. Summers, of the School of Milling and Baking Technology, conducted by the *Operative Miller* of Chicago:—

No. 1.—Kansas hard winter wheat flour.
No. 2 —Illinois soft winter wheat flour.
No. 3.—"Oriental," a spring wheat flour.
No. 4. A standard commercial mixture.

The digestion mixtures usually contained 1 per cent of the original material as their final concentrations, and all the results here recorded have been calculated to this basis. The polariscopic readings are all recorded as read on a Schmidt and Haensch half-shadow saccharimeter reading percentages of *d*-glucose in a 200 mm. tube. The interior of the loaves was used for digestion, either in the form of approximately one-inch cubes or broken down completely by grinding in a porcelain mortar, except where otherwise stated. This grinding does not disrupt the starch granules. In the experiments with cubes, which are not disintegrated by saliva, the results have been corrected for the amount of liquid removed for the separate readings. The digestions were carried out by mixing the materials at 25° and placing them in a water-bath contained in an asbestos-lined air oven maintained at 37°. This procedure was adopted to simulate the conditions of normal digestion *in vivo*, the chilling effect of ingested food being observable for several hours. For the separate readings 25 cc. of the mixture were pipetted out into a beaker containing 2 cc. of a 1 per cent solution of arsenic acid. This mixture was then filtered and the polarisation read on the filtrate. When the starch granules begin to disintegrate (that is, after four or five hours) the fragments tend to run through the filter. Except where otherwise stated the polarisations have been corrected for the optical activity due to the sugars in the bread suspension by polarising the filtrate from a suspension of inch cubes at the end of half an hour. Under these conditions most of the sugars but no dextrins enter the solution, and but little dextrin enters the solution even when the bread is completely broken down. The polarisations are also corrected for the optical activity of the diastoid and the takadiastase. The saliva and ptyalin were optically inactive. Takadiastase attacks both starch and gluten, and also slowly changes the maltose formed from the starch into *d*-glucose. The apparent acidity of the different materials used for digestion was obtained by titrating after half an hour the filtrate from broken down bread suspensions with 0·02/N potassium hydroxide and phenolphthalein, the recorded results having been corrected for the apparent acidity of the distilled water used in making the suspensions.

Table I. gives the polarisation of digestion mixtures made with the breads just described, the bread being in the condition known as "fresh" at the time of the digestion, except where otherwise stated. "Fresh" bread is that baked late in the day for sale next day. Where the same bread was tested after different periods of fermentation the digestion experiments were carried out simultaneously in the same water-bath. Three grms. of the bread in cubic form were placed in the enzyme solution, the final volume being 300 cc. The bread floats throughout the experiment.

These results show, for hard and soft wheat flours, that the time of fermentation of the dough makes no appreciable difference in the digestibility when varied over a range of 400 per cent, nor does such variation appreciably affect the acidity. They show further that the starch of the soft wheat digests nearly three times as fast as that of the hard wheat, the spring wheat and the commercial mixture acting approximately like the soft wheat. The digestion coefficients given in the table were obtained by dividing the polariscopic reading at the end of one-half hour by 1·20 as an approximate average maximum.

The effects produced by the use of yeast which has begun to ferment owing to bacterial activity are marked in the cases of the bread from soft wheat and that from the "oriental" brand, the former being greatly accelerated, the latter retarded. Each of the breads made with spoiled yeast had a bitter taste. The ingestion of a small amount of one of these breads almost immediately caused a burning sensation in the stomach, which lasted for ten hours, at the end of which time it was relieved by the ingestion of soda. Hence their digestion *in vivo* might differ still more than is here indicated for their digestion *in vitro*.

That the difference in the digestibility of the breads from hard and soft wheat flours is due wholly to differences in the amount of gluten these breads contain (8 per cent and 6 per cent respectively) is shown by the results in Table II., obtained by grinding in a mortar some of the pulp of the pulp of the same loaves of bread used in obtaining the foregoing results. The duplicate determinations were made on the same suspension after standing three days in a glass-stoppered bottle, preserved by toluene.

The starch under these conditions in reality digests about as fast as boiled starch, as judged by the iodine colorations and the polariscopic readings (*infra*).

Other factors, such as slight variations in the acidity of the mixtures, in the temperature of mixing the digestion materials, and in the temperature at which the solutions were read on the polariscope, exerted no appreciable effect.

The following results were obtained with three commercial breads, broken down under water just enough to cause the pulp to sink—a degree of disintegration approximately equal to that produced by normal mastication. The readings are uncorrected for the original polarisations, since these were obtained on the pulp just described instead of on the undisintegrated pulp, snd hence the solutions contained appreciable amounts of dextrins:—

Table III.

Bread No. :—	5.	6	7.
Time of digestion (hours).			
0·5	1·12	1·10	1·04
1·5	1·11	1·26	1·28
3·0	1·35	1·22	1·34
23	1·29	1·18	1·24
Normal acidity ..	0·00018	0·00015	0·00012
Original polarisation	0·28	0·20	0·13

These results show that the disintegration of the gluten was sufficient to permit the digestion of the starch to the same extent as that in the breads ground up to flotation. That this agrees closely with the rate of digestion of freshly boiled starch is indicated by the results contained in Table IV. The rice starch used in these experiments was boiled five minutes in approximately 2 per cent solution. The concentration of dry (120°) starch in the digestion mixtures was 0·863 per cent. Table IV. also contains data on the digestibility of a home-baked bread (made with hard wheat flour) and of another commercial bread. The interior of the loaf of these two breads was rasped on a horse-radish grater into fragments about 3 mm. in diameter. The results given in two of the columns were obtained on the same pulps air-dried. The results are not corrected for the original polarisations of the solutions. The starch at its final dilution polarised 0·64, but this seems to be mostly due to dextrins (as the amyloses filter out), which immediately digest, so that this correction should not be applied to the observed readings.

The initial maximum in the polariscopic readings obtained with the starch is due to the presence of a small amount of dextrins in the solution, even with 1 : 7 saliva, so rapid is the hydrolysis of the amyloses present. This may conveniently be shown with iodine after filtering off the rose-amylose provided a preservative has been added to prevent the digestion of the erythrodextrin during filtration.

If the polarisations given for the starch be divided by 1·726 they become directly comparable with all the other results recorded in this paper, on the assumption that the breads contained 50 per cent of starch, since all are calculated to 1 per cent of the original material for the final concentration in the digestion mixture. This maks the values for the starch even at the start, when the solution contained dextrins, only slightly higher than the corresponding values obtained with disintegrated bread pulp (Table II.).

The colorations of the digesting starch with iodine-water show clearly the progress of the digestion of different ingredients in the starch. The original blue colour was partly due to amylodextrin; the red colour given at the end of one hour with iodine in small amount was due to rose-amylose, the dextrins and amylose having been nearly all changed into maltose; by the end of four hours the amylopectin and the rose-amylose were all digested; by the end of five hours the amylocellulose had digested sufficiently to disintegrate the walls of the starch granules (already disrupted by boiling), so that their fragments came through the filter-paper, the mixture now containing red-amylose, requiring a large amount of iodine for the production of its iodide; by the end of twenty four hours the amylocellulose was nearly all digested. The absence of any maltase (*infra*) is to be noted.

The low digestibility of the air-dried bread is probably attributable to the setting of the gluten during the drying, thus rendering the starch more difficult for the enzymes to get at rather than to any change in the starch, as surmised by Neumann (*Zeit. ges. Getreidcw.*, 1914, vi., 119; *Chem. Abs.*, ix., 2554. Confirmed by direct experiment after complete disintegration of the gluten by grinding). The home-baked bread was much more palatable than the commercial breads, but the polarisations show no reason therefor.

That the source and amount of the enzymes make but little difference for moderate variation in amount in the rate of digestion of starch is indicated by the following results, obtained with the same bread pulp and the same starch solution, and the enzymes indicated in Table V. Fernbach and Wolff (*loc. cit.*) found that doubling the concentration of malt extract had no effect on the rate of digestion: —

TABLE V.

Time of digestion. Hrs.	1 p.c. rice starch.		1 p.c. home-baked bread.		
	1 p.c. diastoid.	1 p c taka-diastase.	1 p.c. com'l. ptyalin.	1 p.c. diastoid.	1 p.c. taka-diastase.
0·00		(2·4) (*a*)			
0·50		1·91	(0·47) (*a*)	0·43	0·40
0·75			0·62		
1·00	2·62	1·70		0·72	0·48
1·75			0·96		
2·00	2·42	1·65		0 92	0·47
2 75			1·06		
3·00	2·46			1·17	0·48
3·75			1·14		
4·00	2·42	1·51			0·46
4·75			1·22		
5·00	2·48	1·43			0·45
6·00	2·48				
7·00	2·50	1·35			0·44
24	2 70	1·18			
25	2·60				
26	2·64	1·16			0·44
29					0·45
122		0·92			0·22

(*a*) Extrapolated.

The continuous fall in the readings obtained by the use of takadiastase is noteworthy. The initial value for the starch digestion was obtained by extrapolation, although the maximum must lie somewhere between time 0 and time 0·5 hour. The maximum obtained by extrapolation must be near the true maximum the solution would have shown, however, and agrees approximately with the values obtained by the use of diastoid.

The reason for the steady fall in the polarisation obtained with takadiastase and starch is that the takadiastase contains maltase, as is well known (Daish, *loc. cit.*, 2054), so that the maltose slowly hydrolyses into *d*-glucose. The final value obtained (asymptotically) after 122 hours equals 38·3 per cent of the initial (extrapolated) value, in close agreement, considering all the circumstances, with the theoretical value 39·8 per cent, based on the assumption that the initial optical activity was due to maltose and the final value was due to *d*-glucose, obtained by use of the formula—

$$\text{Rotation of } d\text{-glucose} = \text{rotation of maltose} \times \frac{360}{342} \times \frac{52{\cdot}5}{138{\cdot}3},$$

where 52·5 is the specific rotatory power of *d* glucose, 138·3 the specific rotatory power of maltose, and 360 the molecular weight of two molecules of *d* glucose.

The one-half hour reading obtained by the action of takadiastase on bread also agrees fairly well with those obtained with other enzymes, although the actual amylase present in any of the preparations used was but a small indefinite percentage of the total weight of the enzyme material. These results, therefore, together with the great activity shown by very dilute saliva, seem to indicate that the rate of digestion does not vary appreciably for moderate variations in the amount of enzyme present. Two influences in this case (takadiastase on bread) tend to diminish the polariscopic readings—first, the slow hydrolysis of the maltose to *d*-glucose; second, the digestion of the gluten, with the elimination of levorotatory substances. The value after 122 hours is only 19 per cent of the average maximum polarisation (1·20) of 1 per cent bread preparations.

Takadiastase does not completely digest the amylocellulose even on long standing (122 hours), if it digests it at all; that is to say, if the residue is boiled at any time after the digestion mixture no longer gives any colour with iodine-water (end of the digestion of amylopectin and rose-amylose) it will on cooling give a deep blue with iodine-water.

Conclusions.

1. The specificity and complexity of starches is confirmed.

2. A number of polysaccharides are clearly recognised and differentiated and the existence of two new ones indicated.

3. The three principal ingredients of cereal starches are amylocellulose (the cell walls), amylopectin, and amylose.

4. The amylose, contrary to the contention of Maquenne and Roux, passes through the stages of amylodextrin and erythrodextrin during salivary digestion, but these dextrins digest so rapidly that their presence in the digestion mixture can conveniently be demonstrated only when the enzyme concentration is very low (*e.g.*, 1 : 99). Furthermore, an appreciable amount of achroödextrin enters the solution with ordinary concentrations of saliva.

5. All of the dextrins under ordinary conditions disappear from the solution within fifteen minutes, so that thereafter the further progress of the digestion can be followed by the polariscope, the only optically active substance then present being maltose, if maltase has not been added from some outside source. As the amylose is all digested by this time the further digestion represents action on amylocellulose and amylopectin and their products of hydrolysis.

6. By slow digestion almost the entire amount of amylose present was obtained in solution as erythrodextrin at the end of fifteen minutes. Hence under ordinary conditions the digestion of amylose must be almost instantaneous.

7. Rose-amylose, derived from amylopectin, digests completely in four hours. This has usually been regarded as the end of starch digestion, the rose-amylose being confused with erythrodextrin.

8. The amylocellulose (cell walls) digests only after more than twenty-four hours.

9. The only differences observable in the rate of digestion of bread made from hard or soft wheat, and fermented more or less than usual, were due to the relative amounts of gluten present. When the gluten was broken down the rate of digestion was sensibly the same.

10. The cause of the greater palatability of home-baked bread was not discovered.

11. Various pronounced effects due to fermentation by spoiled yeast were noted.

12. The activity of amylases is not sensitive to small changes of temperature or of acidity produced by the organic acids found in bread, nor does their activity seem to be proportional to their concentrations.

13. It would seem that under physiological conditions most of the amylose must be changed to dextrins in the mouth, and that these dextrins, as well as most of the

amylopectin and its products of hydrolysis, must be digested in the stomach, whereas the digestion of the amylocellulose must take place for the most part in the intestine.

14. Stale (air-dried) bread digests very slowly unless its gluten be completely broken down.

ON THE

QUALITATIVE SEPARATION AND DETECTION (I.) OF TELLURIUM AND ARSENIC AND (II.) OF IRON, THALLIUM, ZIRCONIUM, AND TITANIUM.

By PHILIP E. BROWNING, G. S. SIMPSON, and LYMAN E. PORTER.

I.

In a previous paper from the Kent Chemical Laboratory of Yale University by one of us (Browning, *Am. Journ. Sci.*, 1915, xl., 349) it was shown that an attempt to separate arsenic and tellurium by the addition of magnesium chloride mixture to a solution of ammonium arsenate and tellurite, according to the method of Noyes and Bray (*Journ. Am. Chem. Soc.*, xxix., 137), often resulted in some confusion, due to the fact that a magnesium compound of tellurous acid was precipitated, which interfered with the test for arsenic and removed a considerable part of the tellurium.

The fact that the original hydrogen sulphide precipitate is decomposed by hydrochloric acid and potassium chlorate, and that this oxidation process would probably effect at least the partial oxidation of the tellurium to telluric acid, suggested the investigation of the formation of the telluric acid under these conditions and its effect upon the method. A number of experiments along this line seemed to show that after the treatment of tellurium with hydrochloric acid and potassium chlorate a mixture of tellurous and telluric acids resulted, and that the ammonium tellurate gave a precipitate with magnesium chloride mixture, as has been shown to be the case with ammonium tellurite. From these results we conclude that any attempt to remove tellurium from arsenic by this method is apt to yield doubtful conclusions. We therefore recommend that the tellurium be removed first by the method of Noyes and Bray—viz., precipitation of elementary tellurium by sodium sulphite in dilute hydrochloric acid solution in the presence of potassium iodide. The filtrate from the tellurium should be boiled to remove excess of sulphur dioxide, then treated with hydrogen dioxide, boiled to remove the greater part of the iodide, and then made alkaline with sodium hydroxide and treated with more dioxide to oxidise the arsenic to arsenate. This solution is then acidified to destroy sodium hydroxide and made alkaline with ammonium hydroxide and treated with magnesium chloride mixture, which precipitates the arsenate. The filtrate from the arsenate may be tested for molybdenum by potassium sulphocyanide and zinc in hydrochloric acid solution according to Noyes and Bray. This modification of the original method gave satisfactory results when used by a class of about forty.

II.

The separation of iron in the ferric condition, thallium in the thallic condition, titanium, and zirconium is made by Noyes and Bray (*Journ. Am. Chem. Soc.*, xxx., 481) by dissolving the hydroxides in hydrochloric acid, 1·12 sp. gr., and shaking the solution with ether, the ferric and thallic chlorides dissolving in the ether and the chlorides of titanium and zirconium being being left in the water layer. The iron and thallium are separated by sulphurous acid and potassium iodide and the titanium and zirconium by sodium phosphate in the presence of hydrogen dioxide.

Table I.—*Test for Tellurlum and Arsenic in Hydrochloric Acid Solutions.*

Treatment of solution with Na_2SO_3+KI.

P. Te	F
	Treatment by boiling to remove the SO_2, by H_2O_2 to break up the iodide, by boiling to remove iodine, by excess of NaOH and H_2O_2 to oxidise the arsenic to arsenate, acidifying to remove excess of NaOH, by NH_4OH and $MgCl_2$, NH_4Cl mixture, and filtration.

P. NH_4MgAsO_4	F
Confirmation by $AgNO_3$, forming red brown Ag_3AsO_4.	Testing for Mo by KSCN and Zn in HCl. Red $Mo(SCN)_4$.

Table II.—*Test for Iron, Thallium, Zirconium, and Titanium, taken in the form of Hydroxides.*

Solution of hydroxides in the least amount of H_2SO_4. Treatment with H_2O_2, a red coloration indicating titanium. Treatment with Na_2HPO_4 in the presence of NaOH (see Note) and addition of H_2SO_4 to acidity.

P. $ZrOHPO_4$	F.
	Treatment with NaOH.

P. $\left.\begin{matrix}Fe\\Tl\end{matrix}\right\}$ as hydroxides or phosphates	F.
Solution in H_2SO_4. Treatment with Na_2SO_3+KI, and filtration.	Treatment with H_2SO_4, Na_2SO_3, and Na_2HPO_4, and filtration. P. $TiOHPO_4$.

P. TlI	F.
	Treatment by boiling (to remove SO_2), with H_2O_2 to break up iodide, by boiling to remove iodine, with KSCN. Red coloration indicates Fe.

Note.—This step is to prevent the excess of acid when sodium phosphate is added, which interferes with the ready precipitation of zirconium phosphate. Gentle warming after the addition of the sodium hydroxide gives good results, but in no case should the solution be boiled, and if warmed it should be cooled and treated with hydrogen dioxide before acidifying with sulphuric acid.

This method gives good results but is slow in manipulation and inconvenient and difficult to carry out successfully in the hands of a large class of students lacking experience in such procedures.

As a substitute we present the following method, which has given satisfaction and rapidly obtained results:—

The hydroxides are dissolved in sulphuric acid and hydrogen dioxide added, a red coloration indicating titanium. The solution is then made faintly alkaline with sodium hydroxide, and sodium phosphate is added. Sulphuric acid containing hydrogen dioxide is added to acidity, the latter reagent serving to keep the titanium in the higher condition of oxidation. The zirconium phosphate remains as a precipitate and is filtered off. After the zirconium is removed the filtrate obtained is treated with sodium hydroxide, which precipitates the iron and thallium. After these are removed the alkaline filtrate containing the titanium is acidified with sulphuric acid and treated with sodium sulphite and a little more sodium phosphate, when the titanium phosphate appears. The precipitated hydroxides or phosphates of iron and thallium are dissolved in sulphuric acid, the solution treated with sodium sulphite and the thallous iodide precipitated by potassium iodide. The filtrate from the thallous iodide is boiled to remove sulphur dioxide, treated with hydrogen dioxide, and again boiled to remove iodine and oxidise the iron, and then with potassium sulphocyanide to identify the iron.—*American Journal of Science*, xlii., August, 1916.

MINISTRY OF MUNITIONS OF WAR.

Procedure Affecting Supplies of Materials.

The Ministry of Munitions is desirous of informing manufacturers, merchants, and exporters that the arrangements that have been in force for controlling supplies of steel, tinplates, &c., are to be extended to other materials, and for the convenience of the public an explanation of the above-mentioned arrangements and their extended application is set forth below.

To obtain, whether for home use or export, supplies of copper-wire, cable containing containing copper, Bessemer and open hearth steel, corrugated sheets, tinplates, tinned sheets, terne plates, blackplates, and lead-coated sheets, it will be necessary either to quote a Government contract reference and number if the materials are required to execute a Government contract or to procure a permit reference number and priority classification from the Ministry of Munitions, Priority Branch, 28, Northumberland Avenue, W.C. In applying for such a permit, full particulars of the requirements and purpose should be given. This Government contract reference and number or permit reference and number and priority classification, as the case may be, must be quoted to the suppliers, who are forbidden to deliver any of the aforesaid materials without being furnished with a Government contract number or reference number and priority classification covering the material ordered.

Where one of the following can be quoted to the suppliers no permit reference number and priority classification from the Ministry of Munitions are needed :—

1. Admiralty contract reference and number or Admiralty Priority Section permit reference and number.
2. War Office contract reference and number.
3. Ministry of Munitions contract reference and number.
4. Commission Internationale de Ravitaillement or Commission Française sanction reference and number with Ministry of Munitions priority classification.
5. Board of Trade (Marine Department) (in the case of mild steel only) permit reference and number declaring merchant shipping to be munition work.
6. Post Office contract reference and number (in the case of copper, or copper alloys only).

In the above cases (1 to 6) suppliers on receipt of the contract or permit reference number and a declaration by the customer that the materials ordered are required solely to fulfil the orders covered by the reference number quoted are entitled to deliver on the basis of priority classification A/4 (war work). If a higher grade of priority is required, application must be made to the Priority Branch of the Ministry of Munitions stating the ground of special urgency.

The reference, date, and grade of contract permit or priority classification should be passed on to sub-contractors, if any, so that they, like the main contractor, can quote the necessary particulars referred to above on any orders that may be placed with the merchant, stockholder, or the manufacturer of the materials. This means that once a permit has been granted for a certain plant, such permit covers all parts and materials necessary for completing the plant unless instructions to the contrary are entered on the original permit.

As a general rule, the customer should make the application for permit and priority classification, and not the stockholder or manufacturer of the materials.

References need not be insisted upon in the case of urgent Admiralty telegraphic instructions for immediate repairs to ships.

In cases of machine tool firms and electrical firms the order can be covered by quotation of the reference and date of permit accorded by the machine tool department or electrical branch of the Ministry of Munitions respectively, for the machinery or parts for which the material is ordered.

None of the aforesaid materials can be supplied, except for orders or contracts coming within Class A or Class B; only shell discard quality steel and iron are allowed to be supplied in Class C or Class C Priority Instruction 6. If required for use within the United Kingdom, shell discard quality steel can be obtained without any permit. If for export, shell discard quality steel can be obtained only where the orders have been classified by the Priority Branch, and the reference number of the classification certificate and specific particulars of destination must be quoted to suppliers and the War Trade Department.

In all applications full particulars should be given under the following headings :—

1. A precise description of the articles or materials required.
2. The exact quantities thereof. If required for different orders or purposes the quantities required for each order or purpose respectively. If required for stock or "running account" the minimum quantities needed for a period of three months and the respective quantities in hand at present.
3. The name of the firm or firms with whom the order or orders are or are to be placed, respectively.
4. The respective war, national or other object to be served; and proof of urgency and importance.

A priority certificate is required, even though the goods are merely to be transferred from one branch of a firm in the United Kingdom to another branch of the same firm in a foreign country or British possession.

Merchants, manufacturers, and the general public are earnestly requested to assist the Ministry of Munitions in particular and the nation in general by refraining from applying for permission to obtain the materials mentioned herein unless the same are required for war or other urgent national objects. It is essential that supplies should be conserved for direct war work and work of urgent national importance.—(*Serial Number* C 2872).

Notice in Regard to the Export of Copper-Wire and Cable containing Copper, Bessemer, and Open hearth Steel, or Corrugated Sheets, Tinplates, Terneplates, Blackplates, Tinned Sheets, and Lead-coated Sheets.

1. With a view to conserving supplies of copper-wire or cable, Bessemer and open-hearth steel, corrugated sheets, tinplates, terneplates, blackplates, tinned sheets, and lead-coated sheets, the director of the War Trade Department announces that it has been arranged with the Ministry of Munitions that export licences will not be granted unless a Ministry of Munitions priority certificate (Class A or Class B) permitting manufacture or sale from stock has been obtained, or unless the reference and number of an Admiralty contract or permit or War Office contract for the completion of which the copper-wire or cable, steel, tinplates, &c., are required can be quoted. Export licences will not, as a general rule, be issued in respect of copper-wire or cable, steel, tinplates, &c., for which a Class C certificate is quoted.

2. In the case of allied countries (France, Russia, Italy, Serbia, Portugal, Roumania, Belgium, Japan) priority certificates are only given in very exceptional cases by the Ministry of Munitions unless the application is supported by the Commission Internationale de Ravitaillement, whether the consignment is intended for a Government contract or not. Application should therefore be made direct to the Commission Internationale de Ravitaillement, India House, Kingsway, London, W.C., which, if pre-

pared to support the case, will communicate with the Ministry of Munitions, and arrange for the issue of a priority certificate. If the copper-wire or cable, steel, tinplates, &c., are for Government work and export is allowed, the permits for export will be issued by the Commission Internationale de Ravitaillement. If the goods are not for Government work and the applicant is in a position to quote a priority certificate (A or B) or contract reference and number, he should make an application to the War Trade Department for the grant of an export licence, and if the export is allowed a licence will be granted by that department.

3. In the case of Sweden, Norway, Denmark, Holland, and Switzerland, application should be made in the first instance to the War Trade Department, which, if there is no immediate reason for refusal, will arrange direct with the Ministry of Munitions for the issue of a priority certificate. The applicant should not communicate direct with the Ministry of Munitions, and the priority certificate will be forwarded to the applicant by the War Trade Department with the export licence. This exception does not apply to Bessemer and open-hearth steel nor to corrugated sheets.

4. In the case of all other destinations, including British possessions, application for a priority certificate should be made direct to the Ministry of Munitions, Priority Branch, 28, Northumberland Avenue, S.W. No application for an export licence can be considered by the War Trade Department, unless the number of a Ministry of Munitions priority certificate under Class A or B (or alternatively an Admiralty or War Office contract number) is quoted.

5. A priority certificate is required, even though the goods are already manufactured, and even though the goods are merely to be transferred from one branch of a firm in the United Kingdom to another branch of the same firm in a foreign country or British possession.

6. Applicants are warned that the issue of a priority certificate by the Ministry of Munitions is not a guarantee that an export licence will be issued by the War Trade Department.

7. If exporters have any doubt as to the reliability of the proposed consignee, they are recommended before proceeding to manufacture, to consult the War Trade Intelligence Department, Broadway House, Tothill Street, S.W. (as regards foreign countries in Europe) and the Foreign Trade Department, Lancaster House, The Mall, S.W. (as regards foreign countries outside Europe).—(*Serial Number* C 2873).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 9, 1916.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows: —

"*Methods of Raising a Low Arterial Pressure.*" By W. M. Bayliss, F.R.S.

"*Selective Permeability: the Absorption of Phenol and other Solutions by the Seeds of* Hordeum vulgare." By A. J. Brown, F.R.S., and F. Tinker.

"*On the Toxic Action of Dilute Pure Sodium Chloride Solutions on the Meningococcus.*" By C. Shearer, F.R.S.

"*The Role of the Phagocyte in Cerebro-spinal Meningitis.*" By C. Shearer, F.R.S., and H. W. Crowe.

"*Investigation dealing with the Phenomena of 'Clot' Formations. Part IV. The Diphasic Erosive Action of Salts on the Cholate Gel.*" By S. B. Schryver and Mary Hewlett.

"*Some Photochemical Experiments with Pure Chlorophyll and their Bearing on Theories of Carbon Assimilation.*" By Indvar Joergensen and F. Kidd.

Awards of Medals.

The King has been pleased to approve of the following awards this year by the President and Council of the Royal Society: —

A Royal Medal to Dr. John Scott Haldane, F.R.S., for his services to chemical physiology, more especially in reference to the chemical changes of respiration.

A Royal Medal to Prof. Hector Munro Macdonald, F.R.S., for his contributions to mathematical physics.

The following awards have also been made by the President and Council:—

The Copley Medal to Sir James Dewar, F.R.S., for his investigations in physical chemistry, and more especially his researches on the liquefaction of gases.

The Rumford Medal to Professor William Henry Bragg, F.R.S., for his researches in X-ray radiation.

The Davy Medal to M. Le Prof. Henri Louis Le Chatelier, For.Mem.R.S., for his researches in chemistry.

The Darwin Medal to Professor Yves Delage, for his researches in zoology and botany.

The Sylvester Medal to M. Jean Gaston Darboux, For.Mem.R.S., for his contributions to mathematical science.

The Hughes Medal to Prof. Elihu Thomson, for his researches in experimental electricity.

The Council Election.

The following is a list of those recommended by the President and Council of the Royal Society for election to the Council at the anniversary meeting on Nov. 30:—

President—Sir J. J. Thomson, O.M., M.A., D.Sc., LL.D.

Treasurer—Sir A. B. Kempe, M.A., D.C.L.

Secretaries—Prof. A. Schuster, Sc.D., Ph.D., and W. B. Hardy, M.A.

Foreign-Secretary—Prof. W. A. Herdman, D.Sc.

Other Members of the Council—Prof. J. G. Adami, M.D., H. T. Brown, LL.D., Dugald Clerk, D.Sc., Prof. A. R. Cushny, M.D., Prof. A. Dendy, D.Sc., Prof. P. F. Frankland, LL.D., Prof. J. W. Gregory, D.Sc., H. Head, M.D., J. H. Jeans, Major H. G. Lyons, Major P. A. McMahon, D.Sc., Prof. F. W. Oliver, D.Sc., Prof. C. S. Sherrington, M.D., Prof. A. Smithells, B.Sc., Hon. R. J. Strutt, M.A., and R. Threlfall, M.A.

PHYSICAL SOCIETY.

Ordinary Meeting, November 10, 1916.

Prof. C. V. Boys, F.R.S., President, in the Chair.

A paper entitled "*On Diffusion in Liquids*" was read by Mr. B. W. Clack, M.Sc.

The paper contains the results of the experiments described by the author in *Proc. Phys. Soc.*, 1908, xxi., 374; 1911, xxiv., 40; and 1914, xxvii., 56, collected and recalculated in accordance with a theoretical correction recently communicated by Dr. Griffiths (*Proc. Phys. Soc.*, 1916, xxviii., 255).

It is found that in the solutions employed the correction is not considerable, except in the case of the strongest solutions of KCl (2·7 normal), where it amounts to 6 per cent.

The paper contains the corrected theory of the method, and the value of the coefficient of diffusion is tabulated at different limiting concentrations and at various temperatures; it concludes with a new method of calculating the coefficient at a definite concentration from the experimental results, which appears to be more accurate and free from questionable assumptions than previous calculations of a similar nature.

Discussion.

Prof. G. W. O. Howe asked why the concentration was constant at the bottom of the diffusion tube in the author's apparatus.

Prof. Boys thought this was an important point. He presumed that the upper bulb was sufficiently large that for the purposes of the experiment it could be regarded as an infinite reservoir. A steady state would then be maintained by the circulation through the side tubes, dilute solution rising up one into the reservoir, while more concentrated solution passed down the other.

Dr. R. S. Willows asked why the coefficient of diffusion was greater for strong than for weak solutions in the case of some salts, while the reverse was true for other salts.

Mr. Clack, in reply to Dr. Willows, said he did not know of any reason, but Dr. S. W. J. Smith had told him that that was what would be expected from conductivity data.

A paper "*On the Regularity in the Distribution of the Satellites of Spectrum Lines, with a Note on the Structure of the Green Line of Mercury, and Terms of Correction in Using a Concave Grating*," by Prof. H. Nagaoka, was read, in the absence of the author, by Prof. J. W. Nicholson.

The paper describes a further development of the work done by the author and Mr. Takamine on the distribution of the satellites of the mercury lines. The apparatus employed was a Fabry-Perot interferometer crossed with an echelon or Lummer-Gahrcke plate. An account of the theory governing the interpretation of crossed spectra is given.

It is shown that much of the discord between the results of various observers of these satellites is due to the unsatisfactory nature of the principal line as a datum from which to define their positions, and that if the distances be measured from one of the distinct satellites, good agreement is obtained.

If these separations be expressed as differences of wave-number, instead of wave-length, a remarkable symmetry in their distribution becomes apparent. For example, among the satellites of the green line, 5461, can be found three groups of symmetrical triplets, of which the wave-number differences are in the simple ratios 1 : 3 : 12.

Similar results are obtained for other lines, the principal component of λ 4359 being shown for the first time to consist of a triplet, of which the middle component is relatively weak.

A similarity in the distribution of the satellites exists for all the lines examined, and certain wave-number intervals are common to all.

It is observed that the materials given by—

$$l\,\frac{c}{3},\ m\,\frac{c}{4},\ \text{and}\ n\,\frac{c}{5},$$

where $c = 0{\cdot}71$, and l, m, and n are whole numbers, are found among the satellites of the eight lines quoted for $l = 1$ to 4, $m = 1$ to 7, and $n = 1$ to 7.

The possible origin of satellites is discussed in the light of the Zeeman and Stark effects, the magnetic or electric fields being electronic in origin, and many of the results are shown to be consistent with Voigt's theory of the vibrations of electrons in an isotropic, quasi-elastic, electric field. The suggested explanations can only be tentative as yet, pending further development of our knowledge of the theory of the Zeeman effect, and the extension of Sir J. J. Thomson's work on positive rays to a larger number of substances.

The second part of the paper consists of a mathematical investigation of terms of correction in the theory of large-sized concave gratings, which prevent the theoretical resolving power from being realised in practice.

Discussion.

Dr. H. S. Allen thought the paper contained many interesting and important points. That simple numerical relationships had been shown to hold for the separations of the satellites was likely to prove very helpful to those who were trying to solve the constitution of the atom. He was interested in the discussion of the part which might be played by the magnetic fields of atomic origin in these phenomena. He had himself held this idea for some time.

Dr. R. S. Willows did not quite understand the statement made at the beginning of the paper that there was, as yet, no observations of the effect of an electric field on the satellites, in view of the experiments of Stark, Lo Surdo, and others.

Prof. Nicholson, in reply, said he presumed the statement was intended to refer to the mercury satellites only.

SOCIETY OF GLASS TECHNOLOGY.

A large and most enthusiastic meeting was held on Thursday, November 9, in the University of Sheffield, to discuss the formation of a Society of Glass Technology. The widespread interest in the scheme was demonstrated by the presence of representatives of cities as far apart as London, Edinburgh, and Cardiff, whilst every glass-manufacturing district was well represented.

W. F. J. Wood, Esq., B.Sc., of Messrs. Wood Bros., Ltd., Barnsley, was elected to the chair, and the meeting opened with a cordial welcome from the Vice-Chancellor of the University, who stated that he had great pleasure on behalf of the University authorities in offering accommodation to the Society, and that Sheffield had cause for legitimate pride in the knowledge that its University will be the headquarrers of a Society representing such an important industry. He emphasised the fact that this industry among others had suffered in the past owing to its detachment, wholly or partial, from its scientific aspects. The formation of the Department of Glass Technology in the University was serving to remedy this state of affairs, and the inauguration of this Society was a distinct step in the same direction. His sincere hope was that the Society would be an active force not only in this country but throughout Europe, and no efforts must be remitted to make it truly representative of one of the oldest and most beautiful of industries.

Dr. W. E. S. Turner outlined the steps that had led up to the formation of the Society, and spoke of the remarkable response from those interested in glass. Expressions of warm approval and promises of support had been received from all over the country. He pointed out that there was no intention of making the Society a local institution, but that it was in every way a national one. Meetings would be held from time to time in various centres, so that interest would be stimulated everywhere.

The Report of the Provisional Committee was then presented.

After some discussion the report was adopted, and a formal resolution giving actual being to the Society was passed unanimously.

The election of officers for the coming year then took place, and resulted as follows:—

President—W. F. J. Wood, B.Sc.

Vice-Presidents S. B. Bagley; F. Cheshire; Sir William Crookes, O.M., F.R.S.; A. S. Esslemont; Prof. H. Jackson, F.I.C.; S. N. Jenkinson; H. J. Powell; and W. Rosenhain, B.A., D.Sc., F.R.S.

Council—J. E. Barker; W. R. Barker; P. G. H. Boswell, D.Sc.; F. W. Branson, F.I.C.; W. Butler; F. G. Clark; J. Connolly; J. B. Coppock, F.I.C.; J. H. Davidson, M.Sc.; Prof. W. G. F. Fearnsides, M.A.; J. James Hirst; F. Swann; F. P. Wainwright; and A. D. Young.

Treasurer—F. Sweeting.

Secretary and Editor—W. E. S. Turner, D.Sc., M.Sc.

Assistant-Secretary—C. J. Peddle, M.Sc.

It was decided to leave the drafting of the constitution of the Society in the hands of the Council, and also arrangements for future meetings.

It is to be hoped that now this Society has been established it will receive the support of all those interested in glass, either directly or indirectly. Information on any points will be gladly supplied by Dr. W. E. S. Turner, The University, Sheffield, who will welcome enquiries and suggestions.

NOTICES OF BOOKS.

Bulletin of the Imperial Institute. Vol. XIV., No. 2, April—June, 1916. London: John Murray. Pp. 171. Price 2s. 6d. net.

This number of the *Bulletin of the Imperial Institute* contains a long article by the Director on the work of the Institute for India during the last twenty years, and more especially during the thirteen years in which the Institute has been a Government institution. The work of the scientific and technical research department is described in some detail, and accounts are given of the more important commercial products of India which have been investigated from the scientific, technical, or commercial points of view at the Institute. These include drugs, tanning materials and leather, turpentine and rosin, paper making materials, minerals, &c., and it is clear that the Institute is doing valuable work of a thoroughly practical nature.

British Opportunities in Russia. By Louis A. Rojansky. London: The Anglo Russian Translations Bureau, Ltd. Pp. 11. Price 2d. 1916.

This pamphlet contains a most instructive table of imports to Russia from Germany, Austria-Hungary, and the United Kingdom. Making all allowances for the proximity of Germany to Russia the excesses of the values of her imports over those of the United Kingdom are alarmingly high in the case of almost all the commodities tabulated, and the state of affairs revealed by the table is certainly serious from the point of view of commercial prosperity. The author endeavours to explain Great Britain's lack of success, and is no doubt right in his conclusions that it is due to the superiority, not of German goods, but of the methods adopted by Germany's commercial men, who take the trouble to acquire and use a knowledge of the Russian language, of Russian practice, and Russian ideas. The German banks are also often partly answerable for the success of German enterprise in Russia. The opportunity is now open for Great Britain to remedy the present disastrous state of affairs, and it is earnestly to be hoped that the Government and our banks and merchants will avail themselves of this opportunity.

CORRESPONDENCE.

ADJUSTMENT OF CHEMICAL WEIGHTS.

To the Editor of the Chemical News.

Sir,—As one of your readers who asked if it would be possible to reproduce your paper on the "Correct Adjustment of Chemical Weights" (1867), I wish to thank you for the insertion of this paper in the current issue of the Chemical News, and to assure you that it will be of the utmost value to many chemists.—I am, &c.,

Arnold R. Tankard.

City Chemical and Bacteriological Laboratories,
40, Lowgate, Hull, Nov. 14, 1916.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 13, October 2, 1916.

Detection of Small Quantities of Selenium and Distinction from Arsenic.—Jean Meunier.—Selenious acid and selenites in solution are reduced by nascent hydrogen, and are transformed into seleniuretted hydrogen, H_2Se, a gas which is readily decomposed by heat, giving a deposit of selenium. Thus this element behaves like arsenic and can be detected by Marsh's test. When only a trace is present it is possible that confusion may arise. The author has devised another method of detecting selenium and arsenic. It consists in passing a current of sulphuretted hydrogen through the heated solution. A turbidity is thus produced, due to the precipitation of very finely-divided sulphur, carrying down with it the selenium and arsenic (if it is present) as sulphide. The sulphur can be made to agglomerate by keeping the liquid on the water-bath and stirring when necessary. If the sulphur contains selenium it becomes brown, while arsenic sulphides does not affect its yellow colour.

MISCELLANEOUS.

Research Scholarships for Women.—Two scholarships of £75 each are offered by *The Common Cause* (the organ of the National Union of Women's Suffrage Societies) to women who wish to qualify for positions as industrial chemists. Preference will be given to students willing to study at the Imperial College of Science and Technology, South Kensington, or the School of Technology, Manchester. Applicants, who must have a science degree or its equivalent, should send in their names to the Scholarship Secretary, *The Common Cause*, 14, Great Smith Street, London, S.W., giving full particulars of their qualifications and of the course of research which they wish to pursue.

MEETINGS FOR THE WEEK.

Monday, 27th.—Royal Society of Arts, 5. (Howard Lecture). "Coal and its Economic Utilisation," by J. S. S. Brame.

Wednesday, 29th.—Royal Society of Arts, 4.30. "The Internal Combustion Engine," by Dr. Dugald Clerk.

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THE CHEMICAL NEWS

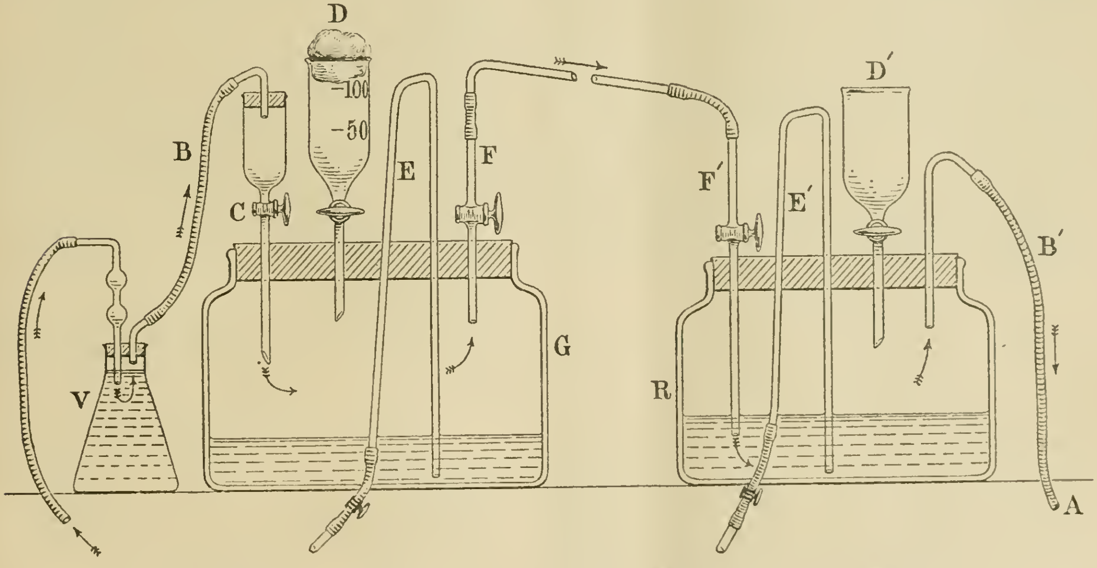
Vol. CXIV., No. 2975.

APPARATUS FOR THE RECOVERY OF BROMINE.

By C. H. COLLINGS.

I. *Object.*

The daily routine work of a clinical laboratory includes the estimation of the urea percentage of urine specimens submitted for analysis. Such urea estimation is usually performed by means of the sodium hypobromite method, and in the course of (say) a year a considerable amount of hypobromite must be thus used and eventually emptied down the sink. As most chemicals now cost 100 per cent more than before the war, it appears to me possible that others may care to save their bromine and their pockets by means of a simple apparatus that I have devised to recover the bromine from used hypobromite. An essential feature about it is that it runs with the minimum of attention and can be attended to by any capable laboratory-boy, thus excluding the need to calculate out cost of skilled labour *contra* market value of Br recovered.



Diagrammatic Illustration of Apparatus for the Recovery of Bromine.

I will now describe the apparatus in detail, with concise instructions for its use.

II. *Apparatus.*

The illustration shows the apparatus set up and working. It consists essentially of a generator, G, connected by a delivery pipe with a receiver, R. The hypobromite waste should first be emptied into a big bottle in the laboratory and allowed to accumulate. It is then introduced into G and commercial HCl added. This displaces the Br from its combination, the Br rising above the fluid in characteristic brown red fumes. A current of air is drawn through the whole length of the apparatus by an aspirator (not shown) connected up at A. This carries the Br fumes into R and discharges them under the surface of a sodium hydroxide solution, made up according to the usual hypobromite formula, minus, of course, the bromine. Here they immediately combine with the NaHO, rapidly transforming it into the yellow hypobromite.

So much for the principle of the thing. I will now give working details, adding for the sake of lucidity that the illustration is purely diagrammatic. The drawing is made as though the generator and receiver were both rolled out flat and the inlet and outlet tubes, &c., placed in a row instead of being, as in reality, grouped together.

Beginning at the extreme left, air under the pull of the aspirator enters the conical glass, V, through the rubber tube leading into the two-bulb tube, emerging under the surface of the fluid, which consists of a solution of caustic soda. It bubbles up through this and passes on through the tube B and inlet tap C into G. (A simpler form, such as F′, can be adopted; that figured lends itself to easy disconnection when putting the apparatus away). A separating funnel, D, marked for 50 cc. and 100 cc., serves admirably for the successive introduction into G of hypobromite waste and commercial HCl. A loose tuft of cotton-wool retains casual fumes. E is a draw-off syphon, closed by a tap at its outlet, to empty G when the HCl action is completed. F is an outlet tube controlled by a tap, and here we pick up the air current again, now charged with Br fumes. It passes on through the delivery tube via F′ into the receiver R. The inlet tube F′ is also controlled by a tap, and its lower end lies beneath the caustic soda (hypobromite formula) contained in R. Here the Br fumes emerge and instantly combine with the NaHO to form sodium hypobromite, evidenced objectively by the initiation of a yellow tinge in the solution and its steady intensification of colour.

D′ and E′ correspond in function to D and E, and need no further description. The air stream, now cleansed of Br, finally emerges from R via B′ on its way to the aspirator, which is connected up with the apparatus at A.

It is necessary, to maintain an effective air-stream, to hermetically seal both bungs with paraffin wax. No leakage should be allowed anywhere.

It is obvious, of course, that the function of V is to prevent any back-push of Br vapour into the air of the room. This undesirable event is effectually provided against, both mechanically and chemically.

Any accidental leakage of bromine at other points can be promptly neutralised by the liberation of ammonium fumes from the 0·880 bench bottle.

III. *Technique.*

Set up the apparatus, see to absence of leakage, connect the aspirator and start it. See that the inlet into V is below the surface of the liquid. Introduce into R through D′ NaHO solution to well cover the bottom end of inlet tube F′. Close D′ tap. Open taps F and F′, keeping tap C temporarily closed. Pour waste into D up to 100 cc.; run into G, close tap, pour commercial HCl into D up to 50 cc., run into G and rapidly close tap. Br fumes instantly rise from the mixed waste and HCl. Cautiously open tap C to full, and all is now under way.

Pour 25 to 50 cc. more HCl into D and replace cotton-wool. Run more of the acid into G from time to time as may be needed. Before admitting it, momentarily close tap C to stop back-rush. A very short time suffices to liberate all the available Br and to aspirate it into R. It is recommended to effect the Br separation in small portions; that is, after the quantity of waste named has been dealt with syphon it off from G before adding a fresh lot. It is now, of course, useless and not worth further preservation.

To test whether Br is still being appreciably given off, close outlet tap F. Back-pressure in V results if evolution is still going on.

In emptying G of treated waste, if fumes are feared run the waste into a beaker or jar holding an inch or two of tap-water. The waste sinks at once in this, the water serving as a screen.

The syphon tubes E and E′ can be brought easily into operation in the first instance by connecting them up respectively with the aspirator direct. This suffices to fill each tube, which can then of course be kept full, ready for next time.

A simple calculation will show the amount of waste needed to furnish sufficient Br for the quantity of NaHO solution in R, allowance being made for dilution of the waste by the urine and for a certain residuum of Br still clinging to combination in G.

NOTES IN REGARD TO TITRATION OF SULPHURIC ACID.

By C. R. GYZANDER,
Chemist to the Cochrane Chemical Company, Boston, U.S.A.

It seems to be a common practice in titrating free sulphuric acid to establish the NaOH titre by some such substance as oxalic acid, acid sodium oxalate, acid potassium phthalate, &c., and phenolphthalein indicator, and then accept this titre with any other indicator that may be deemed proper, on the supposition that all indicators are alike in their action. This, however, is not so, as the following observations will show.

The caustic soda solution used was about N/5, and contained a slight excess of BaO_2H_2 in order to ensure the absence of CO_2 and its interference with phenolphthalein indicator.

The acid used was C.P. sulphuric acid, of which 14·3675 grms. were dissolved in two litres of boiled and cooled CO_2 free distilled water.

The pipettes were of the normal variety, graduated according to the requirements of the Bureau of Standards.

The accuracy of the burettes will be evidenced by the results obtained by them (Table I.).

The end-point for lackmoid, methyl-orange, and dimethylamidoazobenzol appears to be identical under these conditions, and more sensitive than phenolphthalein, but all the indicators are nevertheless proportional to the amount of acid present. The slightly higher result for 10 cc. than what is proportional to the acid present is due to the inability to discern between 6·84 and 6·82 cc. respectively on the burette, graduated in 1/10 cc., and the largeness of the drops, due to the size of the orifice of the tip, which would not deliver drops smaller than one-tenth cc.

Table I.—*Acid for Comparison.*

	Drops.	NaOH solution (cc.).
Acid 10, water 90; total 100 cc.		
Phenolphthalein	5	6·9
Lackmoid	20	6·9
Methyl-orange	5	6·9
Dimethylamidoazobenzol	5	6·9
Acid 25, water 75; total 100 cc.		
Phenolphthalein	5	17·1
Lackmoid	20	17·0 (0·05)
Methyl-orange	5	17·0
Dimethylamidoazobenzol	5	17·0
Acid 50, water 50; total 100 cc.		
Phenolphthalein	5	34·2
Lackmoid	20	34·1
Methyl-orange	5	34·1
Dimethylamidoazobenzol	5	34·1
Acid, 100 cc.		
Phenolphthalein	5	68·4
Lackmoid	20	63·2
Methyl-orange	5	68·2
Dimethylamidoazobenzol	5	68·2

Talbot in the fifth edition of his "Quantitative Analysis," p. 88, quotes Glaser's observations of the variation in end-point of methyl-orange, lackmoid, and phenolphthalein from acid to alkaline reaction with N/10 NaOH. According to his results, 10 cc. of N/10 H_2SO_4 required—

With phenolphthalein	10·1 cc.	N/10 NaOH.
With lackmoid	10·0 „	„ „
With methyl orange	9·9 „	„ „

Repeating my own line of experiments with acid and alkali diluted to about N/10, I obtained the results given in Table II.

Table II.

	Drops.	N/10 NaOH (cc.).
Acid 10 cc., water 90; total 100 cc.		
Phenolphthalein	5	10·2
Lackmoid	20	10·2
Methyl-orange	5	10·2
Dimethylamidoazobenzol	5	10·2
Acid 25, water 75; total 100 cc.		
Phenolphthalein	5	25·4
Lackmoid	20	25·4
Methyl-orange	5	25·4
Dimethylamidoazobenzol	5	25·4
Acid 50, water 50; total 100 cc.		
Phenolphthalein	5	50·8
Lackmoid	20	50·8
Methyl-orange	5	50·8
Dimethylamidoazobenzol	5	50·8
Acid 100 cc.		
Phenolphthalein	5	101·6
Lackmoid	20	101·6
Methyl-orange	5	101 6
Dimethylamidoazobenzol	5	101·6

Under these conditions all the indicators exhibited the same sensitiveness, and the end-points were identical as far as acid consumed is concerned.

The lack of sensitiveness which my indicators exhibited under these conditions compared with those obtained by Glaser must be due to the composition of the indicators themselves, and goes to show that it is not permissible to take things for granted, but one must determine by actual experiment the relation existing between phenolphthalein and whatever other indicators are to be employed, under conditions similar to those of the actual analysis, if phenolphthalein was used in the standardisation of the caustic soda solution.

So, for example, while it would be correct to use the titre established with phenolphthalein on a N/10 NaOH solution for any indicator, it would be wrong to employ 10 cc. portions of N/5 NaOH simply because all the indicators appear to act uniformly in such a case.

The proper thing to do is to establish the titre on any of the larger amounts of solution which indicate a proportional difference between the indicators.

As lackmoid, on account of its sharp change from red to blue, as well as its non-sensitiveness to carbon dioxide, makes the indicator *par excellence* for sulphuric acid, no other indicator should be employed in the titration of commercial sulphuric acid, but as the end-point with lackmoid comes earlier when using N/5 NaOH, the titre established by phenolphthalein must be changed in the ratio $\frac{68{\cdot}4}{68{\cdot}2} = 1{\cdot}00293$ if the titrations are to be identical on identical samples, as of course they should be.

As an example I offer the following analysis of a sample of oleum, which was free from SO_2 but contained a little ferrous sulphate, too small, however, to influence the results, practically speaking. Oleum = 8·0434 grms. per litre, 50 cc. acid + 50 cc. water and 20 drops lackmoid required 42·9 cc. NaOH solution, approximately N/5.

The exact titre of the solution, established with acid potassium phthalate and phenolphthalein, was 0·008077 grm. SO_3 per cc. The lackmoid titre is therefore 0·008077 × 1·00293 = 0·008100 grm. SO_3 per cc., and the results of the titration is—

$$\text{Total } SO_3 = \frac{0{\cdot}0081 \times 42{\cdot}9 \times 20}{8{\cdot}0434} \times 100 = 86{\cdot}40 \text{ p.c.}$$

$$H_2O = 13{\cdot}60$$

$$\overline{100{\cdot}00}$$

$$13{\cdot}60 \times 4{\cdot}4438 = \overset{86{\cdot}40}{60{\cdot}44} \text{ p.c. } SO_3, \text{ equivalent to } H_2SO_4$$

$$\text{Free } SO_3 = 25{\cdot}96 \text{ ,,}$$

Had we accepted the phenolphthalein titre we would have obtained—

$$\text{Total } SO_3 = \frac{0{\cdot}008077 \times 42{\cdot}9 \times 20}{8{\cdot}0434} \times 100 = 86{\cdot}15 \text{ p.c.}$$

$$H_2O = 13{\cdot}85$$

$$\overline{100{\cdot}00}$$

$$13{\cdot}85 \times 4{\cdot}4438 = \overset{86{\cdot}15}{61{\cdot}55} \text{ p.c. } SO_3 \text{ equivalent}$$

$$\text{Free } SO_3 = 24{\cdot}60 \text{ ,,}$$

That is, while we would have cheated ourselves by only 0·25 per cent on total acid by using the lower phenolphthalein titre, we would have underestimated free SO_3 by 1·36 per cent, which is quite a noticeable amount, particularly if oleum is bought and sold on the basis of free SO_3.

The determination of free SO_3 is, however, not always as simple as in this case, since the presence of notable amounts of sulphates and of SO_2 must be established before we may determine water of hydration by difference, or the results in free SO_3 would be too low.

It is also evident that if the NaOH solution is not free from CO_2, its titre, if established with phenolphthalein, will be the more incorrect (that is, too low) the more cc. NaOH are employed in establishing its titre, due to CO_2 interference, and this is undoubtedly the major cause in the often large differences met with in practice when comparing results obtained on identical samples by different operators.

Since few, if any of commercial or works laboratories are provided with constant temperature rooms, the rise and fall in the temperature of the standard solution with the temperature of the laboratory is not always a negligible quantity either.

In the case of the solution quoted, its sp. gr. was 1·00867 at 15° C. and 1·00540 at 30° C. Change in volume in expanding from 15° to 30° C. is therefore $\frac{100{\cdot}867}{1{\cdot}0054} = 100{\cdot}32$ for 100 cc.; that is, the rate of change of volume with temperature is $\frac{0{\cdot}32}{100} \times \frac{1}{15} = 0{\cdot}000213$ cc. per cc. for 1° change in the temperature.

As the solution for the oleum test quoted was standardised and used at 28° C., a cooling to 0° C, would involve a reduction of volume equal to 0·000213 × 8 × 42·9 = 0·07, by which amount the solution used at 20° should be corrected if the results are to be correct. Neglecting this correction the oleum at 20° would appear to contain only—

$$\frac{(42{\cdot}9 - 0{\cdot}07) \times 0{\cdot}0081 \times 20}{8{\cdot}0434} \times 100 = 86{\cdot}26 \text{ per cent total } SO_3$$

$$13{\cdot}74 \text{ per cent } H_2O$$

$$\overline{100{\cdot}00}$$

$$13{\cdot}74 \times 4{\cdot}4438 = \overset{86{\cdot}26}{61{\cdot}06} \text{ per cent } SO_3 \text{ equivalent}$$

Free SO_3 = 25·20 per cent, or a loss of 0·76 per cent which might be avoided by proper allowance for temperature change.

THE SEPARATION OF VANADIUM FROM PHOSPHORIC AND ARSENIC ACIDS AND FROM URANIUM.

By W. A. TURNER.

In a previous paper the determination of vanadium when present in the form of a soluble vanadate has been described (*Am. Journ. Sci.*, 1916 [4], xli., 339). It seemed desirable to make use of this determination for separation of vanadium from some of the common impurities with which it is associated in nature. To this end separations from phosphoric and arsenic acids and from uranium have been attempted, and the following pages are a record of these experiments.

In the separations from phosphoric and arsenic acids the procedure was exactly the same as in the simple determination of vanadium, with the exception that the precipitates required a more thorough washing. This procedure is briefly as follows:—

Portions of about 25 cc. of the metavanadate solution, accurately weighed, were diluted to about 150 to 200 cc. The amount of phosphate or arsenate indicated was added and enough sulphuric acid to make about 1 per cent of the volume. Cupferron (the ammonium salt of nitrosophenylhydroxylamine) was then added in 6 per cent solution with stirring until a slight excess was present, as shown by the appearance of a white precipitate of nitrosophenylhydroxylamine (formed when cupferron comes in contact with an acid solution). Two or three cc. in excess are added and the precipitate is filtered without delay and washed with a 1 per cent solution of sulphuric acid containing a little cupferron. The precipitate after being allowed to drain for a time on the filter is transferred to a platinum crucible, dried, ignited, and weighed as vanadium pentoxide.

The vanadium used was a solution of ammonium metavanadate in distilled water, which when standardised by the cupferron method gave the following result:—

25 grms. NH_4VO_3 solution = 0·1003 grm. V_2O_5.

As sources of phosphoric and arsenic acids disodium hydrogen phosphate and disodium hydrogen arsenate were used. The precipitates were washed fifteen times. Table I. shows how successfully these separations can be accomplished:—

TABLE I.

Grms. NH_4VO_3 solution taken.	Grms. V_2O_5 found.	Grms. V_2O_5 per 25 grms. NH_4VO_3 solution. Found.	Taken.
Impurity added—1·5 grms. $Na_2HPO_4.12H_2O$.			
25·0940	0·1008	0·1004	0·1003
25·0973	0·1006	0·1002	0·1003
Impurity added—1·5 grms. $Na_2HAsO_4.12H_2O$.			
25·0244	0·1006	0·1005	0·1003
25·0841	0·1007	0·1004	0·1003

The separation of vanadium from uranium presents greater difficulty, and in fact as yet a good separation has not been accomplished. For this the same ammonium metavanadate solution used in the previous experiments served. As a source of uranium a solution of uranyl nitrate in distilled water was made. This solution, when standardised by the ammonium hydroxide method (in which ammonium uranate is precipitated by ammonium hydroxide in the presence of ammonium chloride, washed with a dilute ammonia solution containing ammonium chloride, ignited first in the Bunsen burner and then in the blast to U_3O_8), gave:—

25 grms. uranyl nitrate solution = 0·1991 grm. U_3O_8.

When these vanadium and uranium solutions are brought together a yellow precipitate of uranyl vanadate is formed. If sufficient hydrochloric or sulphuric acid is added the precipitate will dissolve. The precipitate appears to be insoluble in ammonia.

It is necessary, therefore, in order to effect a separation of these elements to make the cupferron precipitation in a fairly strong acid solution. In the experiments recorded about 10 cc. of sulphuric acid per 100 cc. of solution were used. The wash-liquid also was a sulphuric acid solution of about the same strength, containing 1·5 grms. cupferron per litre.

Another expedient adopted to accomplish a more complete separation was to place filter and precipitate after thorough washing back in the original beaker, treat with ammonia (which dissolves the vanadium precipitate), then make nearly acid, and cool to 20° before bringing to acidity. After dilution, acidification, and the addition of a little more cupferron bring down the vanadium, which after filtration and washing is obtained in fairly pure form.

The uranium in the filtrate was determined by the ammonium hydroxide method.

In this way the results given in Table II. were obtained:—

TABLE II.

Grms. NH_4VO_3 solution taken.	Grms. $UO_2(NO_3)_2$ solution taken.	Grms. V_2O_5 found.	Grms. U_3O_8 found.
15·3903	25·1603	0·0683	0·2013
20·2137	20·2317	0·0905	0·1610
20·2757	19·0602	0·0904	0·1513

Grms. V_2O_5 per 25 grms. NH_4VO_3 solution. Found.	Taken.	Grms. U_3O_8 per 25 grms. $UO_2(NO_3)_2$ solution. Found.	Taken.
0·1109	0·1082	0·2000	0·1991
0·1119	0·1082	0·1990	0·1991
0·1115	0·1082	0·1985	0·1991

—*American Journal of Science*, xlii., 109.

COLOUR STANDARDS AND COLORIMETRIC ASSAYS.*

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(Concluded from p. 249).

TABLE XI. throws some light on the interesting character of these permanganate-dichromate blends. Because of their instability we have so far employed them only when we found that the "Co-Fe-Cu" or "Co-Cro-Cu" blends did not furnish the desired shade of colour. We hope, however, in the future to study them at greater length. At this time we merely point out that the results as shown in Table XI. prove that the blends required dilution before they would match the tints of the nitrite tests. These dilutions were prepared by first making a blend from N/1000 permanganate and N/100 dichromate solution, and then diluting to the desired intensity of colour. The Lovibond readings appear in Table XII.

TABLE XI.—*Lovibond Readings of the Permanganate-dichromate Blends.*

Mn-Cr blend.	Red.	Yellow.	Blue.
Read soon after mixing.			
1—11	0·7+0·1	5·0+1·6	−0·5
2—10	1·0	5·0+0·7+0·1	−0·5
3—9	1·6	5·0+0·4+0·1	−0·2
4—8	2·0	5·0+0·1	−0·1
5—7	1·0+1·3	4·0	−0·1
6—6	1·8+1·0	1·8+1·0	−0·1
7—5	1·8+1·3	1·9+0·1	−0·1
8—4	2·0+1·6	1·3+0·1	−0·1
9—3	3·0+1·5	0·7	−0·1
10—2	5·0	0·1	None
11—1	5·0+0·4	−0·3	+0·1
Read one day after mixing.			
1—11	0·7+0·1	5·0+1·6	−0·5
2—10	1·0+0·1	4·0+1·6+0·1	−0·5
3—9	1·6	4·0+1·6	−0·3
4—8	2·0+0·1	5·0+0·2	−0·3
5—7	1·0+1·5	4·0	−0·2
6—6	2·0+0·4	1·9+1·0	−0·6
7—5	3·0+0·2	2·0+0·2	−0 6
8—4	2·0+1·5	1·0+0·7	−0·4
9—3	4·0+0·4	0·7+0·1	−0·4
10—2	5·0	0·4	−0·2
11—1	5·0+1·0	−0·1	None
Read two days after mixing.			
1—11	0·4+0·1	5·0+2·0	−1·0
2—10	1·0	5·0+1·6	−0·7
3—9	1·5	5·0+0·7+0·1	−0·5
4—8	1·9+0·1	5·0+0·1	−0·3
5—7	1·0+1·3	4·0+0·1	−0·3
6—6	1·6+1·0	3·0+0·2	−0·5
7—5	3·0+0·2	2·0+0·4+0·1	−0·4
8—4	3·0+0·4+0·2	1·9+0·1	−0·2
9—3	4·0+0·2	1·0	−0·4
10—2	4·0+0·4	0·4+0·2	−0·3
11—1	5·0	+0·2	None

Since the dilutions of the "Mn-Cr-15—1" blend seemed to us to be the best matches for the tint produced in the nitrite tests, we prepared four nitrite tests for final matches, using reagent No. 1, and obtained the Lovibond readings given in Table XIII.

Two observers independently matching as "unknowns" the colours obtained in these nitrite tests with the "Mn-Cr-15—1" dilutions, both sets being in Blake bottles, arrived at the concordant results given in Table XIII.

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* From *Journal of Industrial and Engineering Chemistry*, viii., No. 4.

TABLE IX.—*Comparative Lovibond Readings.*

Nitrogen content.	Half hour after mixing. Red.	Yellow.	Blue.	Two or three hours after mixing. Red.	Yellow.	Blue.
1 : 3,000,000	5·0+2·0+1·5	−0·7	−0·2	5·0+4·0+1·5	−1·3	−0·7
1 : 5,000,000	5·0+1·6	−0·4	None	5·0+1·9	−0·4	None
1 : 10,000,000	4·0	None	+0·4	4·0	None	+0·3
1 : 12,000,000	3·0+0·2	None	+0·2	The second readings were identical with the first.		
1 : 14,000,000	1·0+1·8	None	+0·2			
1 : 16,000,000	1·0+1·5	None	+0·2			
1 : 18,000,000	2·0+0·1	None	+0·2			
1 : 20,000,000	1·9	None	+0·2			

TABLE XV.—*Effect of varying Amounts of Reagents on Vanillin Tests.*

Drops bromine water.	$FeSO_4$ solution. Cc.	Shortly after mixing. Red.	Yellow.	Blue.	One or two hours after mixing. Red.	Yellow.	Blue.
Vanillin solution 1 : 20,000.							
5	1	None	0·7	1·6	0·2	0·7+0·1	1·5
6	1	None	0·7+0·1	1·0+0·7	0·2	1·0+0·1	1·9
7	1	None	1·0+0·1	2·0	0·2	1·0+0·1	1·9+0·2
5	2	None	0·7	1·6	0·2	0·7+0·1	1·5
6	2	0·2	0·7	1·6	0·2	0·7+0·1	1·0+0·7
7	2	0·2	1·0+0·1	2·0	0·2	1·0+0·1	2·0
Vanillin solution 1 : 50,000.							
5	1	None	0·6	1·0+0·1	None	0·6	1·0+0·1
6	1	None	0·6	1·0+0·2	None	0·6	1·0+0·1
7	1	None	0·6	1·0+0·2	0·2	0·6	1·3
5	2	None	0·6	1·3	None	0·6	1·3+0·1
6	2	None	0·6	1·3	0·1	0·7	1·6
7	2	None	0·6	1·3+0·1	0·2	0·7	1·0+0·7

TABLE XII.—*Lovibond Readings of* "Mn-Cr" *Fluids.*

Blend.	Dilution. Per cent.	Red.	Yellow.	Blue.
17—1	25	1·3	None	0·1
	30	1·6	None	0·1
	35	1·8	None	0·1+0·05
	40	2·0+0·1	None	0·2
	100	5·0+0·4	−0·4	0·1
16—1	25	1·3	None	0·1
	30	1·6	None	0·1
	35	1·9	None	0·1
	40	1·9+0·2	None	0·1
	100	5·0+0·4+0·1	−0·4	0·1
15—1	30	1·6	None	0·1
	35	1·6+0·2	None	0·1
	40	2·0+0·1	None	0·1
	45	1·9+0·4	None	0·1
	50	1·9+0·7	None	0·1
	55	1·6+1·3	None	0·1
	60	1·8+1·5+0·1	−0·1	0·2

TABLE XIII.—*Lovibond Readings and* "Mn-Cr" *Matches of Nitrite Tests.*

Nitrogen content.	Lovibond reading. Red.	Yellow.	Blue.	Mn-Cr-15—1 matches (per cent). First observer.	Second observer.
1 : 20,000,000	1·8	None	0·1	30	30
1 : 18,000,000	1·8+0·1	None	0·2	35	35
1 : 14,000,000	2·0+0·2	None	0·2	40	45
1 : 10,000,000	1·9+1·0+0·2	−0·2	None	55	55

Comparison of Tables XII. and XIII. show clearly that matches in Blake bottles agree closely with those obtained by the Lovibond method. Curiously, however, there is rarely an absolute agreement between them, although the difference is within the limits of visual error,

Vanillin.

We first tried the vanillin method given in *Bull.* 107, Bureau of Chemistry, U.S. Department of Agriculture; it may be outlined as follows:—Fifty mgrms. of vanillin are dissolved in 25 cc. of alcohol, and the solution is made up to 100 cc. with water; this solution therefore contains 1 part of vanillin in 2000. Two cc. of this standard are diluted with 30 or 40 cc. of water, 3 or 4 drops of bromine water added, and enough freshly prepared ferrous sulphate solution to produce a maximum bluish green colour; thereupon enough water is added to make a total volume of 50 cc. This coloured dilution therefore has a vanillin content of 1 : 50,000, and is supposed to be of the same tint as any other vanillin solution of the same strength prepared in the same way. We tried several solutions of various proportions of vanillin, and also treated them with varying amounts of reagents, but our experience with this test was highly unsatisfactory, and we consider it unreliable.

We therefore confined ourselves to tests by this method of only two strengths of vanillin, 1 : 50,000 and 1 : 20,000, preparing the solutions from three different samples of vanillin which were on hand, and which are designated as Nos. 1, 2, and 3 in Table XIV.

Endeavouring to see if solutions of three samples of equal strength would be of uniform colour when all were treated in the same manner, we carried out one test of each solution in the two strengths, 1 : 50,000 and 1 : 20,000. In each of these tests we used 4 drops of bromine water and 1 cc. of ferrous sulphate solution, excepting in the last test, when we used 5 drops of bromine water instead of 4. It is plainly seen that the vanillin tests produced uniformity of colour, *only when identical amounts of reagents were used*, regardless of the amount of vanillin in solution. When the amount of bromine water was increased by only 1 drop there resulted an increase in colour value, as is shown by reading of sample No. 3, 1 : 20,000. The five tests that had been treated with 4 drops of bromine water and 1 cc. of ferrous sulphate solution were given to two observers as "unknowns" for the purpose of being arranged in the order of colour intensity, but as all had the same tint neither observer could tell which were the vanillin dilutions 1 : 20,000 and which the 1 : 50,000.

The effects of varying amounts of the reagents were then tested with the results given in Table XV., which show that the intensity of colour produced in the official vanillin test depends principally upon the amount of reagents used and not upon the amount of vanillin present. We therefore abandoned this method, and turned to the one proposed by Folin.

TABLE XIV.—*Lovibond Readings of Solutions of Three Samples of Vanillin.*

Sample No.	Vanillin content.	Red.	Yellow.	Blue.
Readings taken half hour after mixing.				
1.	1 : 50,000	None	0·4+0·2	1·0+0·2
	1 : 20,000	None	0·4+0·2	1·0+0·2
2.	1 : 50,000	None	0·4+0·2	1·0+0·1
	1 : 20,000	None	0·4+0·2	1·0+0·3
3.	1 : 50,000	None	0·4+0·2	1·0+0·1
	1 : 20,000	None	0·7	1·5+0·1
Readings taken two or three hours after mixing.				
1.	1 : 50,000	None	0·4+0·2	1·0+0·2
	1 : 20,000	None	0·4+0·2	1·0+0·2
2.	1 : 50,000	None	0·4+0·2	1·0+0·2
	1 : 20,000	None	0·4+0·2	1·0+0·3
3.	1 : 50,000	None	0·4+0·2	1·0+0·1
	1 : 20,000	None	0·7	1·3+0·3

Folin's Vanillin Assay.—Directions for the preparation of the reagent used and for the manipulation followed in this assay were taken from the *Journal of Industrial and Engineering Chemistry* (1912, iv., 670), and may be outlined as follows:—The phosphotungstic-phosphomolybdic acid reagent used is made by placing in a flask with reflux condenser 100 grms. pure sodium tungstate and 20 grms. phosphomolybdic acid, followed by 100 grms. 85 per cent phosphoric acid and 700 cc. water. The mixture is then boiled over the open flame during one and a-half hours, and is allowed to cool, after which it is filtered, if necessary, finally diluting to 1000 cc. with water. This solution has a vanillin content of 1 : 10,000. Five cc. of it are placed in a glass-stoppered cylinder, and 5 cc. of the phosphotungstic-phosphomolybdic acid reagent are added. After mixing well and letting stand for five minutes the fluid is diluted to 50 cc. with a saturated solution of sodium carbonate. After standing for ten minutes the blue colour of the fluid, which contains 1 part of vanillin in 100,000, is observed.

We prepared standard solutions from two samples of vanillin. Each was diluted to three different strengths representing 1 : 100,000, 1 : 150,000, and 1 : 200,000 respectively. When these solutions were tested and read with the tintometer (Table XVI.) we found that the two original vanillin samples gave the same colour effects for equal strengths of dilution, and that the colour produced was proportional to the amount of vanillin present.

TABLE XVI.—*Lovibond Readings of Folin Vanillin Tests.*

Vanillin content.	Red.	Yellow.	Blue
Solution No. 1.			
200,000	0·3	0 2	2·0
1 : 150,000	0·4+0·2	0·4+0·1	1·6+1·0
1 : 100,000	1·0	0·7+0·05	3·0+0·7
Solution No. 2.			
1 : 200,000	0·3	0·3	1·9
1 : 150,000	0·4+0·1	0·4+0·1	1·5+1·0
1 : 100,000	1·0	0·7+0·1	2·0+1·5

We found excellent colour matches for these tests in blends from our N/50 "Co-Cro-Cu" standard coloured fluids. These blends were then diluted and examined in the tintometer with the results given in Table XVII.

TABLE XVII.—*Lovibond Readings of* N/50 "Co-Cro-Cu" *Blends.*

Blend.	Dilution (per cent).	Red.	Yellow.	Blue.
2—2—8	50	0·2	0·2	1·0+0·4
	60	0·2+0·1	0·2	1·6
	70	0·2+0·1	0·2	1·9
	80	0·2+0·1	0·2	2·0+0·1
	90	0·2+0·1	0·2	1·5+1·0
	100	0·4	0·7	2·0+1·6
3—3—10	50	0·3	0·2	1·0
	55	0·3	0·2	1·0+0·05
	60	0·3	0·3	1·3
	70	0·3	0·3	1 6
	80	0·4	0·4	2·0+0·1
	90	0·4+0·1	0·4+0·1	2·0+0·4
	100	0·4+0·1	0·4+0·1	1 9+1·0
2—2—10	60	0·2	0·2	1·8

Comparing the tests and the blends as "unknowns" in Blake bottles we found that the vanillin dilution 1 : 100,000 matched the "Co-Cro-Cu" blend 3—3—10, 100 per cent, that vanillin dilution 1 : 150,000 matched "Co-Cro-Cu" blend 2—2—8, 70 per cent, and that vanillin dilution 1 : 200,000 matched "Co-Cro-Cu" blend 2—2—10, 60 per cent. Second readings of the vanillin tests are not given, since the colour, after half an hour, was so changed that the readings were worthless.

While the Folin vanillin test is more satisfactory than the official method it leaves much to be desired. In either test a slight variation in the amount of reagent added makes too great a difference in the colour to permit it to be an accurate method of analysis. We believe the Folin test for vanillin to be a good one, but think it needs considerable experimental work before it can be called perfectly satisfactory.

Uric Acid.

After experimenting on several proposed colorimetric tests for uric acid we found the most satisfactory one was that published by Riegler in which phosphomolybdic acid is the reagent employed (*Zeit. Anal. Chem.*, 1912, li., 466).

The standard solution was made by adding 0·1 grm. of Kahlbaum uric acid to the same quantity of sodium bicarbonate, and dissolving in water to make a total volume of 100 cc. This represented a uric acid content of 1 : 1000. The test was carried out as follows:—One cc. of the standard uric acid solution was mixed with 2 cc. of 10 per cent solution of phosphomolybdic acid in a glass-stoppered cylinder; after mixing thoroughly, 7 cc. of 5 per cent solution of sodium phosphate were added, and then the well-mixed liquid was diluted with water to make 30 cc., the uric acid content of the finished fluid being 1 : 30,000. We also made similar blue fluids containing uric acid, 1 : 40,000 and 1 : 50,000. The colour produced in these tests was similar to that obtained in the vanillin tests, but much more permanent. It was no trouble to obtain a second reading with the tintometer after the lapse of one hour. The results of readings are given in Table XVIII.

TABLE XVIII.—*Lovibond Readings.*

Uric acid.	Reading.	Red.	Yellow.	Blue.
1 : 50,000	1st	0·2	0·05	1·5+1·0
	2nd	0·2	0·1	1·3+1·0+0·1
1 : 40,000	1st	0·2	0·1	2·0+1·3
	2nd	0·2+0·1	0·2	3·0+0·1
1 : 30,000	1st	0·4+0·1	0·2+0·05	3·0+1·3
	2nd	0·4+0·2	0·2+0·1	4·0+0·1

Excellent colour matches in Blake bottles were obtained for these tests with our standard "Co-Cro-Cu" coloured fluids. The uric acid fluid 1 : 50,000 matched our blend of "Co-Cro-Cu" 2—2—8, 80 per cent; the one diluted to 1 : 40,000 matched the straight N/50 blend of "Co-Cro-Cu

2—2—8" without any dilution, while the one diluted to 1 : 30,000 had greater intensity of colour than had the straight N/50 blend. We therefore prepared dilutions from our N/10 "Co-Cro-Cu" fluids, and found a proper match for the uric acid 1 : 30,000 in a blend of "Co-Cro-Cu, 4—3—12, 30 per cent," prepared from the N/10 standards.

As noted in some of the other tests exact matches, when the fluids were viewed in Blake bottles, were not the same as the corresponding Lovibond readings. For comparison therefore we will state that the Lovibond readings of the "Co-Cro-Cu" matches were:—N/10 "4—3 12, 30 per cent"—*red* 1·0+0·2, *yellow* 0·4+0·1, *blue* 4·0; N/50 "2—2—8, 100 per cent"—*red* 0·4, *yellow* 0·7, *blue* 2·0+1·6; N/50 "2—2—8, 80 per cent"—*red*—0·2+0·1, *yellow* 0·2, *blue* 2·0+0·2.

Salicylic Acid.

Colorimetric tests on solutions of salicylic acid were made according to directions given in *Bull.* 107, Bureau of Chemistry, U.S. Department of Agriculture. The standard solution is prepared by dissolving 0·1 grm. of salicylic acid in 100 cc. of water, this representing a salicylic acid content of 1 : 1000; 1 cc. of this solution is placed in a glass-stoppered cylinder, and is diluted with water to 50 cc.; a few drops of ferric chloride solution (0·5 per cent) or ferric alum solution (2 per cent) are then added, and after mixing the fluid takes on a bluish colour suggestive of lavender. In experimenting with this test we found that the ferric alum solution produced a deeper colour than did the same amount of ferric chloride solution. This was to be expected, however, since a given amount of a 2 per cent ferric alum solution contains more iron than does the same amount of ½ per cent ferric chloride solution. In comparing tests of equal strength where the amount of metallic iron in each reagent used was equal, we obtained equal colour values. To a solution containing salicylic acid 1 : 50,000 we added 9 drops of 0·5 per cent ferric chloride solution, and compared the resulting colour with that produced in a solution of the same salicylic acid content to which were added 4 drops of the 2 per cent ferric alum solution. The tints were exactly the same.

Desiring to determine the effects of various amounts of the ferric reagents on the salicylic acid reaction, Lovibond readings were taken as shown in Table XIX. Finding that the colour produced by the ferric chloride solution was more permanent than that of the ferric alum solution we thereafter used only the former.

Table XIX.—*Effect of varying Reagents on Salicylic Acid Tests. (Ferric Solution).*

Reagent.	Drops.	Red.	Yellow	Blue.
		Salicylic acid 1 : 50,000.		
Alum ..	4	2·0+0·1	0·1	0·7
Chloride	4	1·6	None	0·4+0·1
Chloride	9	2·0+0·1	None	0·7+0·1
		Salicylic acid 1 : 25,000.		
Alum ..	4	3·0+1·8	0·1	1·6
Chloride	4	2·0	0·1	0·7+0·1
Chloride	9	3·0+1·8	0·1	1·6+0·1

A standard solution was prepared from crystallised salicylic acid. A small quantity of this was dissolved in 1 cc. of alcohol, and then diluted with water to 1 : 10,000. From this a 1 : 50,000 solution was prepared, and to 50 cc. of the latter 9 drops of ferric chloride reagent were added. The Lovibond reading of the resulting fluid was:—*Red*, 2·0+0·1; *yellow*, none; *blue*, 0·7+0·1; which is exactly the same reading as that obtained from the standard solution of the other sample of salicylic acid, each test being of the same strength and treated with the same amount of the same reagent.

As subsequent tests showed that the minute quantity of alcohol present had no effect on the colour results we suggest that in preparing the salicylic dilution, the acid be dissolved in a small amount of alcohol, as directed above, in order to facilitate solution.

Table XX.

	Red.	Yellow.	Blue.
	N/10 Ferric chloride.		
1 cc. in 50 cc. ..	2·0	None	0·7+0·1
2 cc. in 50 cc. ..	2·0+	None	0·7+0·1
1 cc. in 100 cc. ..	1·9	None	0·7+0·1
2 cc. in 100 cc. ..	2·0	None	0·7+0·1
	N/20 Ferric chloride.		
1 cc. in 50 cc. ..	2·0	None	0·7+0·05
2 cc. in 50 cc. ..	2·0	None	0·7+0·1
1 cc. in 100 cc. ..	1·9	None	0·7+0·01
2 cc. in 100 cc. ..	2·0	None	0·7+0·05

Two standard ferric chloride solutions of different strengths were then prepared—N/10 and N/20 and the colours produced on different volumes of salicylic acid solution 1 : 50,000 gave Lovibond readings as per Table XX. These figures suggested the use of 1 cc. of N/10 ferric chloride reagent to 50 cc. of solution containing salicylic acid in tests of this kind, and we prepared to match the colours with our "Co-Cro-Cu" N/50 blends. Finding the 7—1—5 and 6—1—5 blends the best matches, these were diluted and examined in the tintometer with the results given in Table XXI. Comparison of these results with those given in Table XIX. shows that the "Co-Cro Cu" blends "7—1—5, 65 per cent," and "6—1—5 per cent," have practically the same Lovibond readings as the coloured fluids resulting from the salicylic acid dilution 1 : 50,000 being treated with the ferric chloride reagent, and the identity in colour of these three fluids was further established by matching as "unknowns" in Blake bottles.

Table XXI.—*Lovibond Readings of* N/50 "Co-Cro Cu" *Blends.*

Dilution (per cent).	Red.	Yellow.	Blue.
	7—1—5 blend.		
60	1·8+0·1	None	0·4+0·1
65	2·0+0·1	None	0·4+0·1
70	2·0+0·2	None	0·4+0·2
	6—1—5 blend.		
60	1·6+0·2	None	0·4+0·2
65	1·9+0·1	None	0·7+0·1
70	2·0+0·2	None	0·7+0·2

Phosphates.

We tried both phosphoric acid and sodium phosphate with the regular ammonium molybdate reagent used in qualitative analysis, and studied the colour produced. The standard phosphate solution represented a P_2O_5 content of 1 : 2000. To 5 cc. of this in a glass-stoppered cylinder were added 2 cc. of nitric acid and 4 cc. of a 5 per cent solution of ammonium molybdate, and the mixture was then diluted with water to 50 cc. The finished fluid represented P_2O_5 (1 : 20,000), and the colour obtained was a pure yellow that was perfectly matched by our N/50 ammoniacal dichromate standard fluid diluted to 15 per cent; *i.e.*, the colour of a mixture of 15 cc. of the N/50 ammonium dichromate standard fluid and 85 cc. of water. The Lovibond reading of the P_2C_5 solution (1 : 20,000) was:—*Red*, none; *yellow*, 1·0; and *blue*, 0·05; while that of the N/10 dichromate fluid (15 per cent) was *red*, none; *yellow*, 1·0; and *blue* 0·05. Solutions having a P_2O_5 content of 1 : 10,000 were then tried with the same reagents, but the resulting solution became cloudy within five minutes. We then tried the test, using 4 cc. of nitric acid instead of 2 cc., but although the liquid remained clear, the colour was lighter than it was in the previous tests with solutions having a P_2O_5 content of 1 : 20 000. This evidently another test in which exact quantities of reagen must always be employed.

MONAZITE, THORIUM, AND MESOTHORIUM.*

By KARL L. KITHIL.

Introduction.

The monazite industry in the United States has been practically at a standstill since 1906, principally for the reason that monazite could be mined and obtained cheaper from Brazil, where large deposits are found and exploited along the seacoast and in the interior. Formerly part of the monazite mined in the States of North and South Carolina was used for the manufacture of thorium nitrate in this country and part of the production was sent to Germany. It seems an opportune time to call attention to the monazite deposits in the United States, as the imports of thorium nitrate are at present curtailed. There is reason to believe that a more general manufacture of thorium nitrate may be developed in this country. It may be many years before supplies of the nitrate from Europe can be depended upon.

There are deposits of monazite in several of our States, and with the knowledge that a valuable product—mesothorium—can be made as a by-product from the residues of thorium nitrate manufacture the industry may be developed in this country and should pay well. Mesothorium is used successfully in therapy in the same manner as radium.

With these facts in view the following description of the occurrences of monazite in the United States, the uses to which its products can be put, and the methods of mining and treatment has been prepared by the Bureau of Mines with the purpose of aiding more efficient utilisation of radioactive minerals.

Properties of Monazite.

Monazite is an anhydrous phosphate of the rare earths, especially cerium, lanthanum, neodymium, praseodymium, yttrium, and erbium, and contains also a small percentage of thorium. So far its content of thoria only gives the mineral its commercial importance, although a market is being developed for some of the other rare earths in special types of electrodes for arc lamps and in the flaming arc. The content of thoria in monazite is small and varies from a fraction of 1 per cent to about 12 per cent, although monazite containing less than 3½ per cent of ThO_2 cannot be used successfully in the manufacture of thorium nitrate, which is the important chemical product necessary for the manufacture of incandescent gas mantles. In this manufacture the thorium is mixed with 1 to 2 per cent of other nitrates of the rare earths. References to the percentage of thoria in "monazite" generally apply to a sand containing about 92 to 95 per cent of true monazite; such sand is sold in the market on the basis of its content of thoria at a fixed price per unit.

Monazite possesses radioactive properties strong enough to affect a photographic plate and to be measured in the electroscope. The activity of the sand is due to its content of mesothorium and radium.

The specific gravity of monazite varies from 4·9 to 5·3. It has a hardness of 5, is somewhat brittle, and can be easily pulverised.

Nearly all of the monazite brought to the market is of a yellowish, resinous colour. The Brazilian monazite of the coast lands appears to have a more uniform shade of colour and size of grain than the monazite from the interior. The region from which monazite from the Carolinas has been mined can often be determined by its colour alone. Carolinian monazite ranges from yellowish to brownish, greenish, and greyish in colour.

Occurrence of Monazite.

Monazite is usually found in the gravel of small streams or bottom lands, but sometimes it is also found in the soil of hillsides. In Brazil it occurs also in the beach sands of the coast. In places it is found in small crystals in gneiss, granite, and pegmatite (crystalline) rocks.

As these rocks become disintegrated, the crystals are washed into the creeks and streams, and, together with other heavy sands, are deposited in the beds of such watercourses. They are thus concentrated in the gravel by the natural flow of the water; the lighter clay and quartz sand being carried away. On the coast of Brazil the monazite from the crystalline rocks of the coastal mountains is concentrated in strata by the waves of the sea. The mountain sides are washed down by the strong waves at high tide and during storms.

In some places, especially Norway, monazite is embedded in thin layers of mica (biotite) in strata or, in places, in mica schists. Such monazite is usually of high grade, but, on account of the enormous masses of rock material that have to be handled and crushed before concentration, these deposits cannot be considered of commercial importance. The proportion of monazite in these rocks averages perhaps 0·01 per cent.

Where Monazite is Mined.

Monazite has thus far been mined successfully only in North and South America—in North America, in the Carolinas and in Idaho, and in South America in Brazil. The Brazil deposits occur along the coast of the States of Bahia and Espirito Santo, and also less abundantly on the Parahyba River in the States of Rio de Janeiro and Minas Geraes. Other coastal lands in the State of Rio de Janeiro have also been worked. Deposits of monazite sand have been found, too, in Swaziland, Africa, as well as in Ceylon and in Australia. In Jekaterinburg, Russia, it occurs in native rock and placers. It has also been exported from Travancore, India.

In the United States, occurrences of monazite are known in many other States than the Carolinas, but it is probable that the deposits in Idaho and the Carolinas alone are of importance commercially.

Brazil has furnished the bulk of monazite for commercial use. Little has been mined elsewhere since the enormous price cut in the earlier part of 1906, as the workings in the Carolinas have been gradually abandoned. For some years past Brazil has furnished all of the monazite for the gas-mantle industry for both Europe and the United States.

History of Production of Monazite.

Although generally known to interested persons, a short history of the development of production and final overproduction of this once rare mineral may be warranted.

The first monazite used in Europe for chemical purposes was brought at great expense from Sweden and Norway.

About 27 years ago John Gordon, an American, found monazite on the coast of Brazil, in the State of Bahia, and brought the mineral in large quantities to Hamburg. The supply was sufficient to furnish the thorium industry of the entire world with monazite at a comparatively low price. Mr. Gordon obtained a monopoly of the Bahian monazite sands.

At that time the manufacture of thorium nitrate in Europe as a speciality was confined to a few large chemical firms in Germany and to the Welsbach Co. in Vienna. These were the only firms that provided the European market with thorium nitrate. They also sent large quantities of the nitrate to the United States. The American Welsbach Co. early manufactured thorium nitrate from sands mined in the Carolinas, a protective duty of 6 cents per pound making this possible, as the mining of monazite in this country is more expensive than in Brazil.

First German Thorium Convention

Late in 1902 Mr. Gordon entered into an agreement with the four largest German manufacturers and with the Austrian manufacturer by which he agreed to furnish monazite at a price of 150 dols. per metric ton and a percentage of the profits from the manufactured nitrates. With this agreement a close combination was formed which prevented other thorium manufacturers from acquiring any of the mineral mined by Mr. Gordon. The combination was known as the German Thorium Convention, which, after the conclusion of the agreement with Mr. Gordon, immediately raised the price of thorium nitrate 100 per cent.

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* *Technical Paper* 110, U.S. Department of the Interior, Bureau of Mines.

Mr. Gordon's supply came from the coast lands of Bahia, near Prado, Brazil, and he exported the sands for a long period without interference. Finally the Brazilian Government became acquainted with the value of the resources and found an old law according to which all of the Brazilian coast lands along the sea and navigable rivers belong exclusively to the Federal Government for defensive purposes. The Government concluded, therefore, that no private individual or State government had the right to mine, sell, lease, or remove any of this property without the consent of Federal authority. In 1903 the Government of Brazil advertised that coast lands in the State of Espirito Santo would be leased to the highest bidder for the exploitation of the sands lying within its territory.

A business man living in Rio de Janeiro made a contract with the Government, but for some reason allowed it to lapse. Finally an engineer obtained the contract for the firm of A. C. de Freitas & Co., of Hamburg, Germany. By the contract the firm mentioned agreed to pay to the Brazilian Government a rental of 50 per cent of the selling price of monazite sand and to export at least 1200 tons annually during the life of the contract.

Second German Thorium Convention.

To avoid interference, the German Thorium Convention arranged, later on, that half of its supply should be furnished by Mr. Gordon and half by the De Freitas Company; and a new convention was formed by the four German chemical manufacturers with Mr. Gordon and the De Freitas Company by which the latter two were to supply the monazite to the four German manufacturers only and were to receive therefor 150 dols. per ton of monazite and a percentage of the profits from the sale of the nitrates.

As a result of the convention other firms in various countries, which had in the meantime begun to manufacture thorium nitrate, were without a supply of raw material and had to depend upon the ashes of spent mantles. Consequently, they made every effort to find and develop new deposits of monazite in Brazil, the Carolinas, and elsewhere. The whole world was searched for rare-earth minerals by their engineers, with the interest and assistance of many governments. The high price for thorium nitrate made it possible to mine monazite in the Carolinas and export it to Germany; thus one German manufacturer—an outsider—received his supply from North and South Carolina. Later, American firms independent of the Welsbach companies began to buy monazite in the Carolinas, and by the competition created for a brief period caused the price for lands and monazite sand to rise to a point highly profitable to the farmers and landowners of the Carolinas.

Causes of Reduced Price of Thorium.

On account of overproduction in thorium, the price for thorium nitrate was suddenly dropped 50 per cent by the convention in the year 1906. The mining of monazite consequently decreased in all localities where the cost of the mining was high, as, for instance, in the Carolinas.

Since 1906 other difficulties have arisen between the Vienna and English Welsbach companies and the German Thorium Convention; and in 1910 the price was further lowered to a point that made the mining of monazite absolutely unprofitable in the Carolinas, and also in the interior of Brazil. The market was flooded with monazite until the outbreak of the European war.

The German Incandescent Gas Light Co. of Berlin has succeeded during the past few years in controlling the largest manufacturers of thorium nitrate in Europe, with the exception of those in France. The German concern controls now both the English and Austrian Welsbach companies, and consequently their thorium nitrate plant in Austria. This combination is the strongest competitor of the so-called Thorium Convention, and the latter has lost much of its power.

Consumption of Monazite.

The world's consumption of monazite is now about 3000 tons per annum. The annual world consumption of incandescent gas mantles is estimated at 330 million. The United States alone, in spite of the development and use of the electric metal-filament lamps, has consumed in the past few years some 80 million incandescent gas mantles as against forty million total before the year 1904.

In the manufacture of such gas mantles about 0·5 grm. of ThO_2, equal to 1 grm. of thorium nitrate, is used per mantle; hence the world consumption of thorium nitrate is 300,000 kilos, equal to 150,000 kilos. of ThO_2 per annum. If monazite is considered to contain 5 per cent ThO_2, with a 90 per cent recovery in the manufacture, 1000 kilos. (1 metric ton) of monazite will yield 90 kilos. of thorium nitrate. The gas mantles are made of 99 per cent thorium and 1 per cent cerium.

Perhaps the best work in regard to the manufacture of thorium nitrate and incandescent gas mantles has been written by Richard Böhm ("Das Gasgluehlicht, Die Fabrikation der Gluehkörper für Gasgluehlicht," Leipsic, 1905; "Die Thorium Industrie," *Chem. Ind.*, 1906, ix.; xxix, 450).

PROSPECTING FOR MONAZITE DEPOSITS.

Prospecting for monazite is similar to a search for gold. The mining pan of the batëa is the most convenient apparatus in which to wash the gravels of the streams and separate the heavier sands, from among which monazite can be easily detected by its peculiar lustre and colour. Sounding rods should be employed if quick estimates are desirable, and if the thickness and composition of the overlying burden in the bottom lands must be established. The concentrated material of the pannings is dried and sent to the chemical laboratory for determination of the content of thoria and other rare earths.

Use of Spectroscope.

It probably is not widely known that the presence of some of the rare earths in monazite can be easily detected by the aid of a spectroscope, a pocket or hand spectroscope being sufficient. Peculiar as it may seem, the presence of rare earths in the monazite samples as taken from the pan can be at once determined by this method. Determination is best accomplished by spreading some of the concentrated sand on a piece of paper or cloth and holding the spectroscope over the sand at a convenient angle, the natural light falling directly on the sand. A fairly broad dark line will appear between the red and the yellow of the spectrum, and another but narrower line will be seen in the green. These dark absorption bands seem to be due principally to the presence of the rare-earth oxides of neodymium, praseodymium, and erbium contained in the mineral. Such spectrum tests for monazite can be safely relied upon when observed by the trained eye. The entire spectrum used is divided into a scale of 63 mm., the first and broader dark line becoming visible between the 13 and 15 mm. lines. The narrow dark line appears between 21 and 22 mm. of the scale.

The spectrum method of testing in the field is most helpful in far-away places, where a laboratory is not available.

MONAZITE DEPOSITS IN NORTH AND SOUTH CAROLINA.

The monazite deposits in the Carolinas cover an area of several hundred square miles east of the Blue Ridge Mountains and extend in a south-west direction. In North Carolina the counties of Cleveland, Burke, Alexander, Rutherford, and Lincoln furnish the richest deposits. In South Carolina the only deposits of value are in the counties of Cherokee and Greenville.

Practically all of the monazite mined in the Carolinas is derived from the gravels in the streams and bottom lands, the miner usually following the old courses of the streams and creeks in the bottoms. The gravels are of greatly varying thickness throughout, and it is therefore difficult to arrive at a true estimate for an average value. From experience, however, it can be estimated that an average thickness of the monazite-bearing gravels is between 1½ and 2½ feet. There are deposits with a thickness of 3 feet and more, but they are of rare occurrence. The top soil in the bottom lands varies on an average from 3 to 6 feet, and on the outer seams of the bottom toward the hillsides frequently increases to a thickness of 7 feet or more. The top soil is barren and consists usually of sandy soil interlined with clays, or is of clayey matter throughout. Hydraulic methods have been tried on some of the richer soil deposits, but without much success.

North Carolina.

In North Carolina deposits of monazite sand are found in Burke County in the Brindletown district. Here monazite is obtained from the hydraulic washings of the gold placers. The content of monazite in the concentrated black sands, however, is small compared with that of the sluicing concentrates of other sections. The monazite in this section after being purified seldom shows a higher content than 3·5 to 3·75 per cent ThO_2. There is considerable magnetite in these sands, and the bulk of the concentrates consists of ilmenite (titaniferous iron).

McDowell County has a number of deposits in the vicinity of Muddy Creek. The occurrence of monazite here is closely similar to that of Brindletown, but perhaps contains less gold in the sand.

In Rutherford County, within a few miles of Rutherford ton, there are a number of deposits that have been profitably worked for some time for both gold and monazite. The gold has usually been extracted by the miner, and the residues further concentrated and shipped for their content of monazite. This district is especially interesting on account of the large area of the wide bottom lands where the gravel bearing monazite and gold is found to a greater extent than in most other sections. The percentage of monazite in the gravel, however, is not large, and these lands have been worked profitably only on account of their gold content, the monazite being obtained as a by product.

Much activity was shown years ago in the vicinity of Ellenboro, extending to Oak Spring and Sandy Run Creek and up as far as Duncan, which is about 18 miles from Ellenboro. The deposits in this region are more or less alike, and the monazite obtained is of good grade and can still furnish considerable quantities of concentrates. Near Ellenboro is a hillside deposit in which monazite is found in a comparatively pure state in the sand of the hillside as well as in the gravels of the bottom lands.

Cleveland County has a considerable area of monazite-bearing gravels, which extend between Shelby and Mooresboro via Fallston to a place called Zite near Carpenters Knob, a well known peak in that section. The deposits around Fallston and in the entire Carpenters Knob region are of great importance, and have furnished monazite concentrates of especially high thorium content. The rough concentrates obtained from many of the streams in that region contain less black sand and garnets than those in most other sections.

There are also fair deposits in Lincoln County about 15 miles north-west of Lincolnton. These deposits can also be reached from Shelby, N.C.

Alexander County has furnished some monazite concentrates, and there is no doubt but that other deposits can be found in that county.

There has been in former years considerable activity also near Hildebran, Burke County, where fair deposits of considerable extent have been found.

South Carolina.

Nearly all the monazite-bearing gravel in South Carolina is found north of Gaffney, Cherokee County, and Cowpens, Spartanburg County, and in the vicinity of Greenville, Greenville County, south of the Southern Railway.

There is a considerable area of monazite found in the gravels of the creeks and bottoms in all of these sections, and although there have been obtained considerable quantities of monazite concentrates containing 30 to 40 per cent of monazite, the bulk of the crude concentrates coming from these South Carolina sections have been of the "black sand" variety, containing considerable ilmenite.

Many of these deposits in both North and South Carolina have been described by others.

DEPOSITS IN IDAHO AND COLORADO.

Idaho.

The Idaho monazite deposits and the treatment of the gold-monazite-bearing sands in that State have been well described by Sterrett ("Monazite in Idaho," 1910, p. 898, U.S. Geol. Survey Mineral Resources, 1909), also by Schrader ("An Occurrence of Monazite in Northern Idaho," 1910, p. 184, *Bull.* 430 U.S. Geol. Survey), and the concentration methods for the monazite sand used in Idaho are mentioned in the report of the Idaho inspector of mines for 1910.

The monazite deposits near Centerville and Idaho City, Idaho, seem to be of especial importance. There is no doubt but that considerable monazite will be found in many places in the State, and all the gravels of the deposits contain a considerable amount of gold which makes possible the working of such deposits for both gold and monazite. The gravel beds are considerably thicker than those in the Carolinas, and much monazite should be obtained from the tailings from the old gold washings. It must be remembered, however, that the wages paid to the miners in Idaho are considerable higher than those paid in the Carolinas.

Colorado.

Monazite has been found in the State of Colorado some twenty miles south of Denver in the Newlands Gulch district, where the monazite occurs in some of the gravels, which carry also considerable gold. Monazite is also reported in the Platte Canyon.

DEPOSITS IN BRAZIL.

There are three kinds of deposits of monazite sands found in Brazil, as follows:—

1. Deposits within the marinhas (Government lands).
2. Deposits lying behind the marinhas that are private State possessions or belong to private parties.
3. Inland deposits.

The marinhas extend from points in the State of Rio de Janeiro north through the State of Espirito Santo into the State of Bahia.

The bulk of the monazite is derived from these coast sands in the States of Espirito Santo and Bahia. The monazite sand at some places could in former years be taken off the beach by skimming the surface after each tide, and was pure enough to be shipped in the crude state. In later years, however, the material has been of considerably lower grade, so that oscillating tables have been employed, and some of the sands have been washed in sluice boxes wherever enough fresh water was obtainable. The sluice boxes used are larger and of a different construction than in the Carolinas, and no perforated plate is necessary, as there is no coarse gravel in the beach sands. Electro-magnetic separators have also been used direct. These coast lands, called "marinhas," are the property of the Federal Government for 33 metres inland, measured from the point where the sea waters wash the beach at mean high tide. This method of marking property is uncertain, and has, of course, given rise to disputes when boundaries are established.

At a few places along the coast are strips of monazite-bearing sands, lying directly behind or nor far from the so-called marinhas, and some of these could be worked profitably were it not for the difficulties of proving to the Federal Government that these sands were not taken from the near-by marinhas. One French concern is exploiting such lands near Itabapoana, in the State of Rio de Janeiro, and has exported several hundred tons of the mineral annually for some years. There are several other deposits that could be worked, situated between Gargahu and Itabapoana; but, owing to political influences, no other concerns have thus far been able to obtain concessions.

In the interior of Brazil, monazite occurs in many places, but a fuller description of the localities and deposits will not be given here.

The deposits of monazite in the interior of Brazil are of a formation similar to those in the Carolinas, the small streams and bottom lands containing the only deposits of sands possessing commercial importance.

The contents of monazite in the gravels of the streams and bottom lands averages about 0·25 to 0·3 per cent, a proportion about the same as that in the monazite in the Carolinas. There are richer deposits, however, in several sections.

Along the banks of larger rivers, as, for instance, the Parahyba, great quantities of black sands with traces of monazite are found. Near Sapucia, opposite Benjamin Constant Station on the Central Railway, such deposits have been worked by a French concern. They finally had to stop work at this point and abandon also their openings in the mountainous part of this region.

Many of the inland deposits cannot be exploited on account of the expense of transportation of the product, the deposits being situated many miles from the railroad, and the roads and trails being in such condition that it is often difficult to travel over them even with the mule caravan (troupa). The soft clays in the thickets of the jungle-like forests and the crossing of swamps make travel in many cases almost impossible, especially with a heavy burden laden on the mule's back. The rivers in most sections are not yet navigable. Frequent floods, caused by heavy tropical rains, and the lack of proper labour make difficult continuous operation in the interior of Brazil.

At the present prices of thorium nitrate such lands in the interior cannot be profitably exploited by any known method. When once the large deposits along the coast are exhausted, however, and the price for thorium rises, or if some other uses for the mineral and its rare earth contents are discovered, then these deposits may become available.

(To be continued).

NOTICES OF BOOKS.

Dyeing in Germany and America. By S. H. Higgins, M.Sc. Second Edition. Manchester: The University Press. London, New York, Bombay, &c.: Longmans, Green, and Co. 1916. Pp. viii + 143. Price 5s. net.

The first edition of this book was published in 1907, and consisted of a report of a tour made by the author in Germany and America in 1905-6, in accordance with the terms of the Gartside scholarship of the University of Manchester, of which he was then the holder. He gave in the report a general survey of the state of the dyeing industry in the two countries named, and the book attracted a good deal of attention. The second edition contains much fresh matter which the author has accumulated during his experience as a works chemist and manager, and will be welcomed by the increasing number of commercial men who are interested in the dyeing industry in England. There is much of general interest in it, as, for instance, the accounts of the conditions of life of the employées in the different countries, and the descriptions of the great dyeing centres in America, Lowell, Lawrence, and Fall River, Massachusetts. The author believes that a wrong impression exists as to the state of technical instruction in this country, and he is distinctly optimistic regarding the future of dyeing in England, pointing out that most countries put forward a show of pessimism concerning educational matters. A new chapter has been added on colour production, discussing the present situation, the original chapter being also reproduced in a practically unaltered state.

A Text-book of Quantitative Chemical Analysis. By Alex. Charles Cumming, D.Sc., F.R.S.E., and Sydney Alexander Kay, D.Sc. Second Edition. London: Gurney and Jackson. Edinburgh: Oliver and Boyd. 1916. Pp. xv. + 402. Price 9s. net.

This book is well known as a most trustworthy guide in quantitative analysis; it is well written and illustrated, and the methods chosen for description include all those which have been found reliable in practice and are commonly used. Volumetric analysis is treated first, and electrolytic methods are included as well as gas analysis, water analysis, the determination of molecular weights and the ultimate analysis of organic substances. In the second edition no important alterations have been made, but the text has been revised, and some new processes and examples have been added.

The Norfolk Oil Shales. By William Forbes-Leslie, M.B., F.G.S. London: The Institution of Petroleum Technologists. 1916.

This paper, read at the meeting of the Royal Society of Arts on October 17, contains an account of research work upon the Norfolk portion of the Kimmeridge outcrop. The geology of the oil shale fields of the United Kingdom is discussed at considerable length, and the chemical composition of the shales is described fully, analyses being given of them and of the mineral matter in them. The volatile organic matter, including combined water and organic sulphur, amounts to between 30 and 40 per cent. The oil obtained from the shales is described as golden-black in colour and very fluid, although its specific gravity is 0·942 to 0·960. Highly satisfactory results were obtained in bulk tests, the yield of oil being 40 gallons to the ton, and, moreover, a large proportion of the oil contents was obtained at a very low temperature. The author concludes that a large output of oil could be obtained from the Norfolk end of the Kimmeridge outcrop, and he believes that this basin will add very materially to the oil resources of the United Kingdom.

Fifth Annual Report of the Incorporated English Beet Sugar Pioneer Association. 1916. 24, North John Street, Liverpool.

The report of the council of the Incorporated English Beet Sugar Association is interesting reading and provides plenty of food for reflection. The outstanding feature is the fact that there is no substantial progress to report in the establishment of the industry, although more pioneer work has been done by members of the Association. A short abstract is given of the pamphlet by Mr. T. H. Middleton on "The Recent Development of German Agriculture," and the much quoted (but not by any means too much quoted) table of the comparative results produced by the German and British farmer from each acre of cultivated land is given in full. The Association's valuable educational work is described, and the astonishingly satisfactorily results obtained in the trials of the growth of the sugar beet in Cornwall, the Isle of Man, and elsewhere are tabulated. An appendix gives a number of Press comments on the Sugar Beet Association and British sugar growing, and short directions are given for the growing of the beet. It is impossible to read the report without being struck by the thought that its facts, conclusions, and recommendations are chiefly reiterations of similar statements made in a book first published more than forty years ago ("On the Manufacture of Beet-root Sugar in England and Ireland," by William Crookes; London, 1870, Longmans, Green, and Co), in which the questions of the cultivation of the beet, the extraction of sugar, &c., were treated at length. The Association is, of course, to be congratulated upon having restated these facts, and the responsibility for the disastrous results of ignorance and dilatoriness rests elsewhere.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiii. No. 15, October 9, 1916.

Action of Reagents upon French, Bohemian, and German Glasses. — Paul Nicolardot.—Many French glass-makers have undertaken the manufacture of flasks of thin glass like those from Bohemia or Jena. The author has studied the action of various reagents (water, hydrochloric acid, ammonia, ammonium chloride, and sodium carbonate) upon various specimens of glass, carrying out comparative tests with French, Bohemian, and German products. He found that the French glass was comparable with the best German specimens. Tests of resistance to sudden changes of temperature were also carried out.

Some Hydrocarbons contained in Coal.—Amé Pictet, L. Ramseyer, and O. Kaiser.—A soft coal from Sarre was subjected to extraction on a large scale with benzene, 5½ tons of the coal being used, and the extraction lasting four days. The yield of extraction products was small, amounting to only 0·25 per cent of the material used. It could be increased by finely pounding the coal, but this rendered the subsequent operations difficult. From the extract seven saturated and seven unsaturated hydrocarbons were isolated, and these hydrocarbons which were obtained from the coal at a temperature of 80° were compared with those obtained by distillation *in vacuo* at 450°. It was thus found that of the saturated hydrocarbons of vacuum tar some at any rate exist as such in coal. Distillation under reduced pressure separates them by simple volatilisation, no decomposition occurring. The extracted matter is optically active, though no fraction from vacuum tar is ever active. Hence it must be concluded that a temperature of 450° is sufficient to cause the racemisation of the volatile active substances contained in coal, and thus the materials from which coal has been formed can never have have been raised to this temperature.

Determination of Phenol in Raw Tar Phenols.—René Masse and Henri Leroux.—Raw tar phenols consist of a mixture of water, phenol, cresols, xylenols, and homologues. The chemical properties of phenol and the phenols are so much alike that it is impossible to separate them by simple reagents. On the other hand, it is easy to determine the phenol by first fractionally distilling the liquid and then determining the crystallisation point of each fraction.

Semicarbazones of α-Ketonic Acids. α-Iodocinnamic Acids.—J. Bougault.—The action of iodine and free alkali upon the semicarbazone of phenylpyruvic acid gives the two stereo-isomeric α-iodo-cinnamic acids. The insolubility of the acid potassium salt of the stable acid provides a means of separating them. The stable acid fuses at 160—162° and the labile form at 108—110°. They are both very soluble in alcohol, ether, benzene, and carbon disulphide, very slightly soluble in petroleum ether, and insoluble in water. When treated with zinc and acetic acid they both give ordinary cinnamic acid. When heated on the water-bath with an aqueous solution of sodium carbonate they are slowly transformed into phenyl pyruvic acid.

MISCELLANEOUS.

Obituary.—We deeply regret to announce that Mr. John Howard Spalding passed away on Monday, Nov. 20. Mr. John Howard Spalding has been Chairman and Managing Director of Messrs. Spalding and Hodge, Limited, since its formation. Messrs. Spalding and Hodge have supplied us with all our paper from our first number in 1859.

MEETINGS FOR THE WEEK.

Monday, 4th.—Royal Society of Arts, 5. (Howard Lecture). "Coal and its Economic Utilisation," by J. S. S. Brame.

— Royal Institution, 5. (General Meeting).

— Society of Chemical Industry, 8. "Production of Nitrate of Soda in Chile," by I. B. Hobsbaum.

Tuesday, 5th.—Röntgen Society, 8.15. "Some Remarks upon Pastilles," by Dr. Levy and Mr. Stenning.

Wednesday, 6th.—Society of Public Analysts, 8. "Copying Ink Pencils and the Examination of their Pigment in Writing," by C. A. Mitchell. "Brazilian Oil Seeds," by E. R. Bolton and Dorothy G. Hewer.

— Royal Society of Arts, 4.30. "The Coal-tar Colour Industry," by C. M. Whittaker.

Thursday, 7th.—Royal Society. "The Cytomorphosis of the Marsupial Enamel-organ and its Significance in Relation to the Structure of the Completed Enamel," by J. T. Carter. "Development of the Pancreas, the Pancreatic and Hepatic Ducts in *Tricosaurus vulpecula*," by Margaret Tribe. "The Fossil Human Skull found at Talgai," by S. A. Smith. "The Typical Form of the Cochlea and its Variations," by H. J. Watt. "Structure and Biology of Archotermopsis, together with Descriptions of New Species of Intestinal Protozoa, and General Observations on the Isoptera," by A. D. Imms.

— Chemical Society, 8. "Spinacidene—a New Hydrocarbon from certain Fish-liver Oils," by A. Chaston Chapman. "Nitration of 2-Acetylamino-3 : 4-dimethoxy Benzoic Acid and 3-Acetylamino-1 : 2-dimethoxybenzene," by C. S. Gibson, J. L. Simonsen, and M. G. Rau

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THE CHEMICAL NEWS

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INFLUENCE OF FLUORSPAR ON THE SOLUBILITY OF BASIC SLAG IN CITRIC ACID.

By G. S. ROBERTSON, M.Sc.

Until recently practically the whole of the phosphatic basic slag on the market contained phosphoric acid with a solubility, according to the citric acid test, of from 70 to 95 per cent.

(Note.—To perform this test, 5 grms. of the phosphate is placed in a litre flask containing 500 cc. of 2 per cent citric acid solution. The flask is shaken end over end for thirty minutes in an apparatus making thirty revolutions per minute).

As the result of the work of Wagner it has been generally assumed in Germany, and to a certain extent in this country, that the agricultural value of basic slag is proportional to the solubility of the phosphate in 2 per cent citric acid. The high solubility of the phosphate in citric acid was said to be due to the silica which combined with the phosphate. It was contended that the higher the percentage of silica in the slag the more soluble the phosphate is in citric acid, and that all that was necessary to obtain a highly citric-soluble phosphate was a liberal supply of sand. Collins (*Journ. Soc. Chem. Ind.*, 1915, xxxiv., 10), however, has been able to show that the reverse of this contention holds true.

During the past few years steel manufacturers, particularly those using the basic open hearth process, have been introducing fluorspar into the furnace. Fluorspar produces a much more fusible slag, and greater quantities of lime can therefore be added without making the slag too thick.

The peculiarity of basic slag produced by the use of fluorspar is that the solubility of the phosphate, according to the citric acid test, varies from 20 to 50 per cent instead of from 70 to 90 per cent.

The citric solubility of two of these "fluorspar slags," produced respectively by Messrs. Dorman, Long, and Co. and Messrs. Bell Bros., is given in Table I. Five grms. of each of these slags (fineness 80 per cent) was submitted to five consecutive half-hour extractions with 500 cc. of 2 per cent citric acid.

Obviously the citric acid test, as ordinarily performed—that is to say, one extraction—affords no reliable indication of the solubility of these slags in citric acid. In the case of Dorman, Long's slag, more phosphoric acid is soluble in the second citric acid extraction than in the first. A glance at the ratios which the phosphoric acid and lime dissolving in the various extractions bear to one another, suffices to show that they are fairly constant, whilst the ratios of silica to phosphoric acid in the extractions made from Bell Bros.' slag are so divergent as to suggest at once that the silica does not enter into the composition of the phosphate.

With the object of obtaining further information on these results, two 5-grm. portions of a highly citric soluble basic slag (92 per cent) were calcined with fluorspar in a Fletcher muffle furnace and then submitted to consecutive extractions with 2 per cent citric acid. Portion 1 was calcined for about two hours with 0·5 grm. of fluorspar, and Portion 2 for about four hours with 0·1 grm. of fluorspar. The analysis of the basic slag used is given in Table II.

The solubility of Portion 1 has been reduced from 92 per cent to 29 per cent, and of Portion 2 from 92 per cent to 72 per cent. The results secured with Portion 1 are very similar to those obtained with Bell Bros.' slag, and point to the conclusion that the silica in this portion is not in combination with the phosphate. When the highly citric soluble slag is calcined without fluorspar and extracted with ½ per cent citric acid in order to get the phosphoric acid, lime, and silica gradually into solution, the phosphoric acid and silica dissolving in the various extracts bear a fairly constant relationship to each other, as the results given in Table III. show.

Table I.

Dorman, Long, and Co.'s Basic Slag.

Citric extract.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	Ratio, P_2O_5 : CaO
First	1·61	33·24	17·50	—
Second	2·04	5·27	22·17	1 : 2·58
Third	1·75	3·63	19·02	1 : 2·07
Fourth	1·34	2·66	14·56	1 : 2·00
Fifth	1·01	2·02	10·98	1 : 2·00
Extract totals ..	7·75	46·82	84·23	
Actual totals ..	9·20	52·75	100·00	

Total SiO_2 = 17·10 per cent.

Bell Bros.' Slag.

Citric extract.	P_2O_5, per cent.	CaO, per cent.	SiO_2, per cent.	Per cent P_2O_5 of total.	Ratio, P_2O_5 : CaO.	Ratio, SiO_2 : P_2O_5.
First ..	3·75	26·12	7·10	34·20	—	1 : 0·53
Second	2·41	5·24	1·58	22·00	1 : 2·17	1 : 1·52
Third .	1·76	3·72	0·84	16·04	1 : 2·11	1 : 2·09
Fourth	1·10	2·35	—	10·00	1 : 2·13	—
Fifth..	0·95	2·13	—	8·66	1 : 2·24	—
Extract totals	9·97	39·56	9·52	90·90		
Actual totals	10·97	45·10	20·45	100·00		

Table II.

	Total (per cent).	Citric soluble (per cent).
P_2O_5	17·84	16·40
CaO	48·82	43·16
SiO_2	9·45	8·94

Solubility of phosphoric acid according to citric acid test 92·4 per cent, fineness 88 per cent.

Portion 1.

Citric extract.	P_2O_5, per cent.	CaO, per cent.	SiO_2, per cent.	Per cent P_2O_5 of total.	Ratio, P_2O_5 : CaO.	Ratio, SiO_2 : P_2O_5.
First ..	5·30	22·56	6·00	29·71	—	1 : 0·88
Second	6·31	11·44	0·72	35·37	1 : 1·81	1 : 8·76
Third .	4·31	7·48	—	24·20	1 : 1·73	—
Fourth .	1·22	2·86	—	6·84	1 : 2·34	—
Fifth ..	0·42	0·96	—	2·35	1 : 2·30	—
Extract totals	17·56	45·30	6·72	98·47		
Actual totals	17·84	48·82	9·45	100·00		

Portion 2.

First ..	12·89	33·38	6·58	72·25	—	1 : 1·96
Second	4·12	7·62	0·30	23·09	1 : 2·33	1 : 13·73
Third..	0·82	1·60	—	4·60	—	—
Extract totals	17·83	42·60	6·88	99·94		
Actual totals	17·84	48·82	9·45	100·00		

It would thus appear that one of the effects of fluorspar is to cause the formation of a phosphate which does not contain silica in combination as is the case with high citric soluble slags.

Low citric soluble slags, such as those dealt with, have been used successfully as fertilisers in several parts of this country, and have produced results comparable with the highest citric soluble slags. There has never been brought forward a single reliable piece of evidence in support of the citric acid test. Wagner's work on which the citric acid test was founded has been severely criticised by Soxhlet, who alleged that a great deal of it had been falsified, and it is significant to note that Soxhlet was found not guilty in the libel action which ensued. Unfortunately every conceivable means is still being used by the German slag syndicate and certain agents in this country who sell a high citric soluble slag, to bolster up the citric acid test—a test which, to a certain extent, they initiated.

Table III.—*Analysis of High Citric Soluble Slag.*

	Total (per cent).	Citric soluble (per cent).
P_2O_5	17·02	13·87
CaO	46·12	38·56
SiO_2	12·37	12·37

Solubility of phosphoric acid according to citric acid test, 81 per cent; fineness, 82 per cent.

High Citric Soluble Slag. Extracted with ½ per Cent Citric Acid.

	P_2O_5.	CaO.	SiO_2.	Ratio, P_2O_5 : CaO.	Ratio, SiO_2 : P_2O_5.
Sugar extract (*a*)—					
First	—	1·34	—	—	—
Second ..	—	0·91	—	—	—
Citric extract—					
First	5·19	12·45	3·18	1 : 2·40	1 : 1·63
Second ..	5·12	12·07	3·00	1 : 2·36	1 : 1·71
Third . ..	3·52	8·20	2·00	1 : 2·33	1 : 1·76
Fourth ..	1·26	3·10	0·72	1 : 2·46	1 : 1·75
Fifth	0·52	1·26	0·23	1 : 2·42	—
Extract totals	15·61	39·33	9·13		
Actual totals .	17·02	46·12	12·37		

(*a*) Extracted for four hours with 500 cc. of 10 per cent cane-sugar solution containing 10 cc. of absolute alcohol, in order to remove any free lime.

A very large proportion of the basic slag now produced in this country is of low citric solubility, and it is evident that if ever the citric acid test had any significance, the alteration in the process of manufacture of the slag has destroyed it.

Many thousands of tons of the "fluorspar slag" are produced annually, and form a waste product—one Teeside firm alone produces over 100,000 tons per annum. Certain firms even pay a few pence per ton to have the slag carried out to sea. It is certainly unfortunate that a worthless test should prove one of the obstacles to the extensive utilisation of this very valuable and enormous source of phosphoric acid.

It is worthy of note that in the United States "citric insoluble rock phosphates are used even in preference to high citric soluble slags. In this connection, Table IV., contrasting the citric solubility of a "fluorspar slag" with a sample of Tunisian rock phosphate, is of interest.

Table IV.

	"Fluorspar slag." Bell Bros. Fineness 80 per cent			Tunisian rock phosphate. Fineness 100 per cent.		
Citric extract.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.
First . ..	3·75	26·13	34·20	4·83	14·37	18·48
Second ..	2·41	5·24	34·20	7·81	11·84	29·88
Third ..	1·76	3·72	16·04	5·83	8·84	22·31
Fourth ..	1·10	2·35	10·00	4·40	6·62	16·84
Fifth . ..	0·95	2·13	8·66	2·93	4·30	11·17
Extract totals ..	9·97	39·56	90·90	25·80	45·97	98·68
Actual totals ..	10·97	45·10	100·00	26·13	48·40	100·00

Conclusions.

1. The results clearly show that the citric acid test gives no true idea of the solubility of the phosphate in "fluorspar slags" and affords no guide to its value to the plant.

2. The use of fluorspar in the manufacture of steel by the open hearth process results in the production of a phosphatic slag with low citric solubility. Nevertheless, the slag is completely soluble in citric acid if sufficient time is spent on the extraction.

3. The phosphate or phosphates which the slag contains do not appear to be in combination with silica, and they seem to bear a very close resemblance to those contained in mineral phosphates.

At the present time there is a very big demand for phosphatic manures, and if temporary difficulties, such as lack of railway facilities and shortage of bags, could be to some extent mitigated there is no reason why these low citric soluble basic slags should not be placed on the agricultural market at a tempting price.

The author wishes to express his sincere thanks to Mr. S. Hoare Collins for his invaluable advice and suggestions.

—*Journal of the Society of Chemical Industry*, xxxv., No. 4.

ON THE QUANTITATIVE ESTIMATION OF SMALL QUANTITIES OF SULPHIDE SULPHUR.

By W. A. DRUSHEL and C. M. ELSTON

The methods of estimating sulphide sulphur in common use depend—(1) upon oxidation of the sulphur to the sulphate condition and weighing it as barium sulphate, (2) upon oxidation by means of standard iodine and titration of the excess of iodine with standard sodium thiosulphate, and (3) upon the precipitation of the sulphur by an excess of standard sodium arsenite as arsenious sulphide and titration of the excess of arsenite with standard iodine. These methods all require considerable time for execution, and the first and second methods are not entirely reliable for quantities of sulphide sulphur much smaller than 0·04 per cent. The third method is said to be accurate for quantities of sulphide sulphur as small as 0·0003 per cent, but it is necessary to allow the mixture, after treatment with sodium arsenite, to stand for twelve hours in order that the precipitated arsenious sulphide may be removed quantitatively by filtration before the excess of arsenite is titrated back with iodine.

The object of the present investigation was to develop a rapid method of estimating very small amounts of sulphide sulphur with a fair degree of accuracy. The method is a colorimetric method, and consists essentially of the comparison of the depth of colour of lead sulphide stains obtained from the sulphide sulphur of a given weight of a sample to be analysed with a standard series of stains prepared from sulphide solutions of known sulphur content. A set of stains varying in depth of colour from a faint yellowish brown to black, representing from 0·0002 per cent to 0·004 per cent of sulphide sulphur, may be prepared and used indefinitely for comparison. With a set of standard stains at hand the method has the advantage that within the range given the sulphide sulphur of a sample may be determined with a fair degree of accuracy in less than ten minutes.

Preparation of Standard Set of Sulphide Stains.

The apparatus used for preparing standard stains and for making analyses is very simple. The inner tube of a Liebig condenser, with its larger end about 18 mm. in internal diameter, was cut off 15 cm. in length. The smaller end was drawn down somewhat, rounded, and fitted to a sound cork stopper, which in turn was fitted to a 100 cc. round-bottom flask. The condenser tube then served as a sort of reflux condenser. To the upper and larger end of this tube a filter-paper moistened with a dilute solution of lead acetate was smoothly fitted and tied, so that the steam passing up through the tube and carrying hydrogen sulphide was required to pass out through the lead acetate paper. A similar tube, with the internal diameter of its larger end (about 36 mm.), was also prepared and used for sulphide sulphur samples containing 0·001 per cent or more of sulphur.

A solution of sodium sulphide was made up with pure distilled water and carefully standardised. The solution was then diluted to contain exactly 0·01 per cent of sulphide sulphur. This solution was used for making up standard solutions containing 0·0002, 0·0004, 0·0006, 0·0008, 0·001, 0·002, 0·003, and 0·004 per cent of sulphide sulphur respectively, taking care to use distilled water free from traces of nitrites in making the dilutions. It was found that the more dilute sulphide solutions when made up with ordinary distilled water lost their sulphide content either wholly or in part on standing for several hours in stoppered bottles. This difficulty was obviated by using nitrite-free distilled water in making up the solutions.

Carefully measured portions of 1 cc. to 5 cc. of the standard solutions were pipetted into the 100 cc. flask and 25 cc. of hydrochloric acid of about 0·5 per cent strength were added. The flask was immediately attached to the condenser tube fitted with moistened lead acetate paper as previously described. The mixture was then gently boiled for a few minutes at such a rate that the steam issued not too rapidly from the upper end of the condenser tube. In this way the sulphide sulphur was quantitatively liberated as hydrogen sulphide and evenly deposited as lead sulphide on the moistened lead acetate paper. The undecomposed lead acetate was then washed out, the paper dried, and labelled with the amount of sulphide sulphur present as one of the set of standard stains. In the same way complete sets in duplicate were prepared, ranging in sulphide sulphur from 0·0002 per cent to 0·004 per cent.

In order to determine the accuracy with which sulphide sulphur may be estimated in this way, one of us made up a series of sodium sulphide solutions which the other estimated by the method outlined. The results are given in Table I. The first column shows the amount of sulphide sulphur in the solutions as made up. In the second column are the estimated amounts of sulphide sulphur.

Table I.—*Sulphide Sulphur (per Cent).*

	Taken.	Found.	Error.
1.	0·0025	0·0020	0·0005
2.	0·0015	0·0012	0·0003
3.	0·0006	0·0006	—
4.	0·0004	0·0003	0·0001
5.	0·0004	0·0004	—
6.	0·004	0·005	0·001
7.	0·0000	0·0000	—
8.	0·0002	0·00015	0·00005
9.	0·008	0·009	0·001
10.	0·002	0·0025	0·0005
11.	0·001	0·0015	0·0005
12.	0·0001	0·0001	—

In making these estimations the larger condenser tube was used where a preliminary trial indicated that the amount of sulphide sulphur was equal to or greater than 0·001 per cent. In all other cases the smaller tube was used. The maximum error, depending upon the amount of sulphur present, with the larger tube was 0·001 per cent and with the smaller tube 0·0003 per cent. These errors may be reduced by repeating the determination and taking the mean of several values found. In this way, in the practical applications of the method, the errors may be kept withfn reasonable limits.

Practical Applications.

1. *In Gas Analysis.* The method was used for the estimation of the hydrogen sulphide in the laboratory atmosphere and in illuminating gas. On a day when no hydrogen sulphide generator was being used in the laboratory the air contained barely a perceptible trace of sulphur; on another day, when a class two floors below was using a hydrogen sulphide generator, the amount of hydrogen sulphide in the air of the upper laboratory was found to be 1 part in 5,000,000. Twenty-five litres of air were slowly drawn through a Geissler bulb of the most modern type containing dilute potassium hydroxide solution. This solution was then washed into a measuring flask and made up to the mark with nitrite-free distilled water, and aliquot portions of this solution were used for determining the sulphide sulphur as previously described. The same procedure was used for estimating the hydrogen sulphide in illuminating gas. The colorimetric method gave 1 part of sulphur in 1,000,000 of gas. The same result was obtained by oxidising the larger portion of the solution from the Geissler absorption apparatus with bromine water and weighing the sulphur as barium sulphate. Duplicate determinations on the same illuminating gas gave precisely the same result.

2. *In Coke Analysis.*—The simplest method of estimating sulphur in coke given by Fresenius is to boil 5 grms. to 10 grms. of powdered coke in dilute hydrochloric acid, and to absorb the hydrogen sulphide evolved in dilute potassium hydroxide solution. The sulphur is then oxidised to the sulphate condition by chlorine water or bromine water and weighed as barium sulphate. This method was used as a control to check up the results obtained by the colorimetric method. In this method the hydrogen sulphide was liberated and absorbed as suggested by Fresenius, and aliquot portions of the sulphide containing potassium hydroxide solution were transferred to the distillation flask and the previously-described procedure was followed. A comparison of the results obtained by the two methods on several samples of coke is found in Table II.

Table II.—*Coke Analysis. Per Cent Sulphide Sulphur Found.*

By Fresenius gravimetric method.	By colorimetric method.
0·049	0·050
0·050	0·050
0·026	0·025
0·025	9·026
0·027	0·025

3. *In Paper Analysis.*—Another practical application of this method of determining sulphide sulphur is in paper analysis. In order that tissue paper may be used for wrapping polished metal without producing a tarnish the paper must be relatively free from sulphide sulphur. A weighed amount of paper, 1 grm. to 2 grms., is cut into small pieces and transferred to the distilling flask and digested with gently boiling 0·5 per cent hydrochloric acid, collecting the hydrogen sulphide as lead sulphide on lead acetate paper as previously described. A number of samples of tissue paper were examined, and in those samples which contained sulphide sulphur the amounts varied from 0·0002 per cent to 0·001 per cent. Papers which contained the larger amounts of sulphide sulphur when usdd for wrapping polished silver pieces usually produced a marked tarnish in the course of two or three weeks.

This colorimetric method of estimating very small quantities of sulphide sulphur is very rapid, fairly accurate and has a number of practical applications.—*American Journal of Science*, xlii., 155.

OPIUM ASSAY.

Routine Application of Modified B.P. Method.

By H. P. SHILSTON.

The Aliquot Calculations.

To save time, double the B.P. amount is weighed wet on receipt, and, of course, double amounts are used throughout. Of the lime filtrate 51 cc. is used if the sample is dry (52 cc. if wet); this is taken to equal five-sixteenths of the weighed portion.

Line A—G, *Laboratory Work ; Line* H—R, *Elaborated Arrangement to show Theory ; Line* S—*aa*, *Dowzard Method* (*P. J.*, lxxii., 397 ; lxxi., 909).

Line.	Meaning of figures.	How obtained	Persian.		Chinese smoking.		Extract.		Turkish raw.	
			Block.	Pointed.	Ball.	Tin.	Cloudy.	Clear.	Moist.	Pulv. dry.
A	Weight of 50 cc. sp. gr. bottle *c* filtrate	Got direct.	50·95	50·95	50·80	51·20	50·90	50·60	50·80	50·775
B	Sp. gr. of filtrate		1·019	1·019	1·016	1·024	1·018	1·012	1·016	1·0145
C	Extract, dry per cent weight : volume in filtrate		4·4	3·63	3·41	5·525	4·08	3·20	3·92	3·72
D	Ash " " " "		1·20	0·93	1·012	1·375	0·95	0·65	1·06	0·95
E	Cc. N/10 H_2SO_4 = to morphine in 51 cc. filtrate		15·1	15·3	9·1	21·1	18·45	15·4	25·8	15·8
F	Per cent moisture		11·5	15·0	25·0	21·2	19·4	19·1	21·22	Nil
G	Weight of sample taken		18·3	16·0	13·8	16·0635	9·5	8·236	17·77	16·0
H	Weight of water in sample taken	G × E/100	2·1	2·40	3·45	3·40	1·84	1·57	3·77	Nil
I	Total weight of volume of water present	160 + H	162·1	162·40	163·45	163·40	161·84	161·57	163·77	160·0
J	Grms. total extract in volume of filtrate = total volume of water present	I × C/100	7·13	5·89	5·57	9·03	6·60	5·17	6·42	5·95
K	Weight of volume of filtrate = to I	I × B	165·18	165·48	166·06	167·32	164·73	163·51	166·39	162·32
L	Volume or weight of water in volume of filtrate = I	K − J	158·05	159·59	160·49	158·29	158·13	158·34	159·97	156·37
M	Volume of extract in volume of filtrate = I	I L	4·05	2·81	2·96	5·11	3·71	3·23	3·80	3·63
N	Total increase to I on taking up soluble solids	L : M : : I : N	4·15	2·86	3·00	5·27	3·80	3·30	3·89	3·71
O	Volume equal to sample taken	I + N	166·25	165·26	166·45	168·67	165·69	164·87	167·66	163·71
P	Weight of morphine titrated	E × 0·0285 + 0·051	0·481	0·487	0·310	0·652	0·572	0·49	0·786	0·501
Q	Weight of morphine in weight taken, using O	$\frac{P \times O}{51}$	1·568	1·578	1·012	2·156	1·874	15·83	2·582	1·608
R	Per cent morphine found, using Q	$\frac{Q \times 100}{G}$	8·57	9·86	7·333	13·42	19·73	19·23	14·54	10·05
S	Per cent $Ca(HO)_2$ in ash	D × 1·32	1·585	1·23	1·333	1·816	1·255	0·858	1·400	1·255
T	Volume of $Ca(HO)_2$ in ash	S × 0·48 or $\frac{3}{1{\cdot}44}$	0·76	0·59	0·64	0·87	0·60	0·42	0·674	0·60
U	Per cent extract not $Ca(HO)_2$	C − S	3·20	3·04	2·77	3·709	2·825	2·78	2·52	3·12
V	Volume extract not $Ca(HO)_2$	$U \times \frac{1{\cdot}9}{3}$	2·03	1·92	1·75	2·35	1·79	1·77	1·596	1·97
W	Volume $Ca(HO)_2$ in I	$J \times \frac{T}{100}$	1·23	0·96	1·046	1·42	0·97	0·68	1·097	0·96
X	Volume extract not $Ca(HO)_2$ in I	$I \times \frac{V}{100}$	3·29	3·12	2·86	3·84	2·90	2·86	2·61	3·15
Y	Total volume of filtrate = weight of sample taken	I + W + X	166·62	166·48	167·356	168·66	165·71	165·11	167·477	164·11
Z	Weight of morphine in weight of opium taken	$\frac{P \times Y}{51}$	1·571	1·590	1·017	2·156	1·875	1·586	2·581	1·612
aa	Per cent morphine, using Y	$\frac{Z \times 100}{G}$	8·58	9·96	7·37	13·42	19·73	19·26	14·52	10·07
bb	Volume of filtrate = 5/16 sample taken *ex* O	O × 5/16	51·95	51·64	52·01	52·71	51·78	51·52	52·40	51·16
cc	Volume of filtrate = 5/16 sample taken *ex* Y	Y × 5/16	53·07	52·02	52·30	52·70	51·78	51·60	52·33	51·28

If exact results are wanted, the moisture, &c., is done and the volume calculated as in one or the other methods illustrated in the accompanying table, with the aid of the following formula (based on Farr and Wright's method—*P. J.*, lxxviii, 166), the letters of which are explained below. Only a few of the data in the table are wanted, namely, A to I, excluding D; P is calculated from E.

$$\text{Per cent morphine} = R = \frac{100\ P}{51\ G} \times \frac{100\ I}{100\ B - C}.$$

MONAZITE, THORIUM, AND MESOTHORIUM.*

By KARL L. KITHIL.

(Continued from p. 269).

Mining of Monazite in the Carolinas.

Most of the mining for monazite in the Carolinas is carried out in a primitive way, similar to the old methods of gold mining. The gravel is washed in sluice boxes without riffles, the sands being stirred with a square shovel, with an upward movement toward the head of the sluice box, the sands of higher specific gravity being thus concentrated, whereas the lighter clay and some of the quartz sand are washed away. The gravel dug from the pit is thrown on a perforated plate, which is fastened over the head of the sluice box. The larger stones are removed from the plate. A stream of water (about 18 to 20 gallons per minute) is fed through a spout to the gravel on the screen, and the sand is washed through the holes, about one-eighth of an inch in diameter, in the plate into the head of the box. Usually two men are employed to each sluice box, one digging and lifting the gravel out of the pit to the screen, and the other concentrating the sand by stirring it in the box with the motion described above. With this method much of the finer sand is lost, as the grains of sand vary greatly in size, and the finer heavier grains of monazite are carried away by mechanical action with the lighter and coarser quartz. If the sands are properly sized before being washed, a much better result can be obtained, and practically all of the monazite contained in the gravel or sand can thus be saved.

The sluice boxes are of such construction that easy transportation is possible, a desirable feature, because, as the gravel is worked out in one pit in one or two days' time, the boxes then have to be moved higher up the stream or bottom. It has been found more practical and cheaper to remove the box to the deposit than to bring the gravel to the box. The sluice box is usually brought over the pit, which has been worked out previous to the removal of the box, thereby furnishing, to some extent, a dumping place for the tailings that flow off the end of the sluice box. However, as the amount of tailings washed out during one day is large the so-called "tail raise" must be cleaned out with the shovel several times during the day, the tailings so removed being thrown to one side of the bank of the tail-raise. This is necessary in most instances, as the lands slope only slightly, and in some sections the bottoms and stream beds are almost level.

After the sands have been concentrated in the sluice box the concentrates are often rewashed by an experienced hand, and a further amount of useless material removed. The concentrates are then dried in the sun or in a form of drier—usually made of a piece of sheet-iron with turned up edges—a wood fire being built underneath.

Many of the Carolina mines could not have been exploited had it not been for the fact that the people worked out the mineral on their own account from small deposits during times when no farm work could be done. They seldom figured their time of work, mined out what they could, and brought it to the separating plants, where they were paid in cash at the rate of about 8 cents per pound of pure monazite (machine-cleaned sand). Others were employed by some of the corporations at about 80 cents to 1.25 dols. per day at the richer mines. It was not long, however, before new dealers arrived in the Carolinas, greatly inspired by the high prices which were then paid for the nitrate, who, knowing little of the trade, and with only crude means of judging the content of monazite in the washed concentrates, paid 12, 15, and often as high as 35 cents per pound, based on concentrates containing 92 per cent monazite. This development caused unhealthy competition, which proved fatal to the farmers and small operators, as they went to large expense to produce large quantities of the sand, which they then held for higher prices, but could not sell at all when finally the market for thorium nitrate broke. To-day there is no mining of monazite in the Carolinas.

Milling Methods in the Carolinas.

The deposits are too scattered and are not extensive enough to make practical or profitable the use of sliming and oscillating tables. Other concentrating apparatus of special design can be utilised, and with proper sizing of the material excellent results can be obtained with such machines and methods, as has often been demonstrated by practical tests.

The concentrates produced in the sluice boxes contain 20 to 60 per cent of monazite. An average of about 35 per cent can be considered a conservative estimate as a result of practical experience. The concentrates have to be further refined, and are best treated by electro-magnetic separators, of which the Wetherill-Rowand type has proved to be the most useful to the industry. The testing laboratories of Krupp now use a new type of electro-magnetic separator of the Ullrich type, which treats the material either "wet" or dry. It is reported to have a capacity of about 2 tons of material per hour, which is considerably larger than that of any other type of magnetic separator heretofore known. The Daggett separator has also been used successfully for this kind of concentration.

Electro-magnetic Equipment used.

In the separation of monazite from other minerals and its gangue materials, electro-magnetic methods were found to be most efficient (see C. G. Gunther, "Electro-magnetic Ore Separation," 1909; see also "Bibliography on Magnetic Concentration" in R. H. Richard's "Ore Dressing," 1909, ii., 832).

Weakly magnetic bodies can be separated from each other by employing highly concentrated magnetic fields. Such separation is made possible on account of the difference in the magnetic permeability of different material. However, the magnetic permeability as a physical property can be fixed only for absolutely pure material, entirely free from any admixtures, as such admixtures of foreign matter influence considerably the magnetic relativity of the material to be treated, and it therefore cannot be applied as a theory in the treatment of most minerals, which always carry a certain amount of impurities. And, furthermore, it is impossible to bring different minerals, by known methods of crushing, grinding, &c., to a uniform size and shape of particles, as further factors, such as amount tested, and whether the charge is packed tight or loose, affect the results, and not even comparatively correct results can be obtained. Only practical tests therefore will satisfactorily determine the best results for ores and minerals, as on most of such electro-magnetic separators the magnetic power can be controlled to the finest points by means of a rheostat. The intensity of the magnetic field must be adjusted for each specific separation of minerals.

The large type of Wetherill separator has been used in the United States and in Brazil for the concentration of monazite. The separator has two magnets of different sizes, one being nearly twice the size of the other. Each of these magnets has two pairs of poles, forming four magnetic fields, and permitting a separation of two products with each magnet. The magnets are best adjusted so that the first pole of the first magnet removes from the sand the highly magnetic material, as, for instance, the magnetite and ilmenite; the second pole of the first magnet extracts the garnets and also the finer grains of ilmenite; the third magnet (being the first pole of the second magnet) removes all of the coarser grains of monazite; and the last pole extracts the finer grains of monazite. At the end turn of the 18-inch rubber belt of the machine the residues are then dropped into a receptacle. This is best arranged in such manner that the residues are dropped from the funnel of the receptacle into the feed box of a small oscillating table, or other suitable means for the wet concentration of the gold and zircon, which are often present in small quantities. Some fine monazite escaping with the non-magnetic material may also be recovered.

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* *Technical Paper* 110, U.S. Department of the Interior, Bureau of Mines.

By-product Separation.

Sometimes the by-products are found to be valuable enough for market, and it is then of advantage to make a still finer separation, which can be accomplished by employing a type of separator with three magnets—giving six magnetic fields—of three different sizes and strengths, the last magnet being the largest and strongest. In this way the poles can be adjusted so that each magnetic field attracts and removes practically the entire amount of one certain kind of mineral contained in the sands, thereby giving six distinct products, besides all of the non-magnetic products, which are separated at the end of the magnetic operation by running the residues over an oscillating table.

Cost of Mining and Milling.

The deposits of monazite sands in the Carolinas are, as has been previously stated, patchy, and not one single deposit is known to be large enough to justify the erection of a large washing and concentrating plant at the mine itself. The magnetic separators are best placed at a point on a railroad, and as nearly as possible in a district central to many deposits.

The percentage of monazite in the gravel averages 0·25 per cent. It will thus be seen that enormous quantities of crude material have to be handled in order to obtain a ton of marketable material—about 400 tons of gravel furnishes 1 ton of monazite. In addition, the quantities of barren overburden which must be removed have to be added. The overburden often averages more than double the amount of gravel to be moved. No monazite in the Carolinas can be mined by present methods for less than 6 to 8 cents per pound of monazite contained in the concentrated material as taken out of the sluice box. This means that to the cost of the mining must be added the cost of further concentration, sacking, interest on investment, amortisation on plant, management, freight, cartage, &c.

One man can dig and remove in nine hours (this being the usual working shift in the Carolinas) about 9 cubic yards of material, including top soil, barren sand and clay, and monazite-bearing gravel.

The wages paid are 1 to 1.25 dols. a day. Therefore if we take for a rough calculation an area of 3 square yards of ground and a depth of soil and gravel of 9 feet, equal to 27 cubic yards, or about 80,000 pounds in weight, the cost would be as follows:—

For digging and removing of barren material and dump, and digging and removing to sluice box of the monazite-bearing gravel, three men at 1.25 dols., one day each, or 3.75 dols.; for rough washing of 9 cubic yards of gravel in sluice box, one man one day, 1.25 dols.; final cleaning up in special sluice box of rough concentrates 0.50 dol.—a total of 5 25 dols.

As the content of monazite in gravel is 0·25 per cent, or about 68 pounds of pure monazite in washed concentrates, the cost is about 7¾ cents per pound of monazite contained in the washed concentrates.

The cost of transportation to the magnetic separator varies according to the distance over which the material has to be hauled, and averages about 4 dols. per ton of monazite in concentrates, making a total cost of 159 dols. per ton of monazite in concentrates. To this has to be added the cost of drying of the crude concentrates, and of electro-magnetic separation. When the plant is running to its full capacity (nine-hour shift), turning out about 3 tons of pure monazite per shift, 10 dols. for treatment, depreciation, separation, and repairs can safely be added to the above amount per ton of monazite. The entire cost of 1 ton of machine-separated monazite, containing 92 to 95 per cent monazite, and about 4½ per cent ThO_2 is therefore 169 dols. at the concentrating plant. To this has to be added the cost of management, commissions, tolls, if any, loading on cars, and freight to chemical plant or port.

Comments on Electro-magnetic Process.

In concentrating monazite sands by the electro-magnetic process, it is essential that great care be taken throughout the entire operation that the strength of the current is the same at all times, as the slightest variation will cause imperfect separation. An impure product and much less of monazite will result unless this precaution is observed, as the monazite will be taken up by the wrong poles. This contingency is more fully illustrated below.

If the strength of current be too great some of the monazite will be mixed with the valueless ilmenite or garnets; or, if the ampèrage be too low, ilmenite or garnets will be carried over to the next following pole, and will then become mixed with the monazite, and, at the same time, too many of the finer grains of monazite will escape in the tailings. The distance between pole magnets must be carefully adjusted, and the number of ampères for each magnet regulated by rheostats for each kind of sand, for every section of the country, or even when from the same section different percentages of monazite and impurities are present (see Table II. *prox.*).

It may be stated that a better result is obtained when the sands are slightly roasted before magnetic separation than if they are simply sun-dried or air-dried. The difference is due to the fact that roasting renders the material more magnetic. It has accordingly been found that the proper adjustment of the ampèrage for magnetic separation is quite different for sands that have been sun-dried than for those dried over the fire.

Other electro-magnetic separators have been used, operating on similar principles, but did not give as high concentrates in one operation as the Wetherill type, although, perhaps, the new Krupp separator may do so. However, some other concentrators have been used with fair results.

By-products usually found in the residues that can be separated by employing an oscillating table are zircon, rutile, gold, and sometimes platinum. Some of the platinum is slightly magnetic, and may be lost during this process of separation.

ESTIMATED MONAZITE RESOURCES.

It is difficult to give even a rough estimate of the quantities of monazite obtainable in the various countries where it occurs. From close calculations, however, it is estimated that the lands in the marinhas along the sea coast of Brazil may yield from 15,000 to 20,000 tons of pure monazite. This does not include coast lands where the deposits have been formed in comparatively short time.

In the interior of Brazil the writer knows of about 18,000,000 tons of monazite-bearing gravel deposits which should yield monazite containing 4½ per cent of thorium oxide, and it can be estimated that these gravels contain 45,000 to 60,000 tons of monazite. No doubt there will be found many other deposits of greater or less extent in the interior of Brazil, but no single deposit in the interior, so far as known, would warrant the erection of a large plant. In sections where several large deposits are found together or near each other a washing and concentrating plant might be profitably established, provided that the price for the monazite obtained were higher than at present (May, 1915), and especially if transportation facilities from the interior to the coast became better.

The amount of purified monazite available in the Carolinas may be conservatively estimated at about 15,000 to 20,000 tons ($4\frac{1}{2}$ per cent ThO_2).

With better methods of mining and refining the monazite, perhaps those deposits could be profitably exploited at the present prices for monazite and thorium nitrate, especially if the mining of monazite were carried on in conection with the manufacture of thorium nitrate and mesothorium.

It is known that attempts have been made to extract the monazite from the native rock, but this operation with even the richest rock known—0·1 to 0·2 per cent of monazite—has proved to be too expensive, and such endeavours have been given up as hopeless.

Duty on Monazite Exported from United States and Brazil.

United States.

There is no duty on monazite exported from the United States.

Brazil.

The duties on monazite exported from Brazil vary greatly, and are as follows :—

Federal Government.—Duty on monazite from the marinhas—situated along the entire coast and navigable rivers of Brazil—is charged at the rate of 50 per cent ad valorem, and is fixed at £30, or about 150 dols., per ton. Invividual States have fixed duties as follows :—

Rio de Janeiro.—65 dols. per metric ton (approximately 21 dols.).

Espirito Santo.—80 per cent of selling value, established to be £25 per ton. This duty is varying, and is subject to reduction when applied for.

Minas Geraes.—12 per cent ad valorem, fixed at £25 per ton, and 25 per cent ad valorem, fixed at £25 per ton, plus £2 specific duty.

Import Duties on Monazite.

The duty on monazite imported into the United States has been 6 cents per pound, but was reduced to 4 cents in 1910, and is now 25 per cent ad valorem

The import duty on mantle ashes is 10 dols. ad valorem.

The import duty on nitrates has been 25 per cent ad valorem.

Examination and Valuation of Monazite Deposits.

The following features should be ascertained in the investigation of monazite deposits for exploitation :—

1. Extent and depth of the monazite-bearing alluvial deposits, sands, and gravels in river beds and bottoms.
2. Amount and character of barren overburden overlying the gravel or sand deposit.
3. The percentage of monazite contained in the raw material to be treated.
4. Percentage of thorium oxide contained in the monazite.
5. Transportation facilities and cost of transportation.
6. Water conditions—rain-fall throughout the year, and water supply for concentrating purposes, and for the boiler.
7. Timber obtainable on or near property for building use, fuel, &c.
8. Depth and character of bedrock.
9. Occurrence and character of clays.
10. Power available.
11. Labour, also conditions for housing.
12. Mining laws.
13. Cost of supplies.
14. Import and export duties.
15. Best-suited methods for exploitation (concentration, &c.).
16. Quantities and value of by-products and methods of obtaining same.
17. Dumping ground.
18. Inclination of surface of property.

These points having been thoroughly determined, and also whether the existent volume of material, together with other conditions, will warrant exploitation and the erection of a plant, it should be concluded from the topographic features which methods of exploitation of the material will be most suitable.

In determining the average extent and depth of such alluvial deposits great care must be taken to ascertain the situation of the old channels of the streams, as many of the deposits in bottom lands are irregular, so that a true estimate of the amount of gravel or sand contained can be given only after thorough testing by way of soundings, and especially by opening test pits at short distances from each other. As the percentage of the mineral contained in the gravels is small and the thickness of the deposit is usually slight, it will be realised that an enormous area of gravel and sand deposit must be within easy reach to insure profitable exploitation. The relation of volume to richness is therefore a most important consideration.

Transportation is a feature that has to be well considered.

In sections in the Carolinas quickly rising streams and sudden torrents have destroyed dams and carried away sluice boxes, implements, and other materials obtained by hard labour. Uncovered deposits have been covered up again with the sands and mud brought from the mountains during such torrents. Rich deposits have also been purchased during favourable seasons, which could ordinarily be worked during short periods only, on account of lack of water or, in winter, hard frozen gravel, the thawing of which was too expensive. Had the conditions been properly studied, much loss might have been avoided.

Careful forethought regarding a dumping ground should be made in all developments for large quantities of bowlders, clay, and tailings are produced. The deposits may become choked because the refuse material is dumped in an undesirable place, causing further work to be abandoned, as the removal of dump material is costly.

Clays give great trouble when present as an overburden or, as is of frequent occurrence in the Carolinas, when mixed in large quantities with the gravel. The removal of the clayey overburden is much more expensive than removal of sandy materials, and when the clay is mixed with gravel washing consumes more time and large volumes of water.

When clay is mixed with gravel particular care must be used in removing it, as much monazite may adhere to it. The clays seldom contain any of the mineral, but the mineral becomes embedded in the outer parts of the clay while lying in the alluvium. The practice of cutting up the clay is useless and wasteful, although this method has been followed by some of the operators. It is sufficient to wash the surface of such clays carefully and then remove them to the dump.

Attempts to remove By products.

Attempts have been made to utilise by-products from Carolina monazite. Twenty tons or more of ilmenite has been shipped to Europe, but could not bear transportation costs. Garnets derived from the separators have been widely offered, but have been found to be of no value as abrasives, the grains being rounded off by the constant friction while rolling along with other sands in the stream beds. The larger particles of garnets obtained by classification, which could have been crushed and thereby had their sharp edges preserved, have been obtained in small quantities only from the monazite sands.

In some sections gold is found in the concentrates. Although the amount so obtained has been small it has paid to put aside the residues after treatment by electromagnetic methods, and then, when sufficient quantities have been collected, to concentrate them on an oscillating table or by some other suitable process. Although the proportion of gold contained in such sands is not great it has been known to have a value of about 200 dols. per 30 tons of monazite, which is equal to about 1½ cents per ton of gravel. This could be considered almost clear profit, as the extraction of the gold from the residues is inexpensive. Monazite sands purchased from gold-mining sections, which have been treated for gold by the miners, have, after the separation of the monazite, yielded a further small amount of the precious metal.

In many sections "black sands" accompany monazite in large quantities.

In this paper methods of treatment in actual use have been described. It is, however, more than probable that small dredges would prove useful in the mining of monazite as they have in the western field for gold.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 23, 1916.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*Corrosion and Electrical Properties of Steels*" By Sir Robert Hadfield, F.R.S., and E. Newbery, D.Sc.

The condition that a metal shall dissolve in an acid with evolution of hydrogen is—

Single potential of metal $+$ over-voltage
$<$ single potential of hydrogen electrode.

All measurements being, of course, made in the given acid.

If therefore we assume that the atmospheric corrosion of a metal is a process similar to that of dissolution in an acid, it should be possible to predict the corrosion resisting power of a given metal by determining its single potential referred to a hydrogen electrode, together with its over-voltage in a suitable electrolyte.

Experiments on a number of special steels have been carried out to test the validity of the above assumption. The over-voltage, single potential, and loss of weight in acid of each specimen was determined and compared with the atmospheric corrosion observed after exposing clean surfaces to the air for ten weeks.

The results showed that the electrical method gives decidedly better estimates of the corrosion resisting powers of steels than the acid method, and although neither method gives reliable estimates in all cases, yet the electrical method appears to rest upon a sound theoretical foundation, and is probably capable of further developments which may result in the formation of reliable corrosion data.

"*Monoclinic Double Selenates of the Nickel Group.*" By A. E. H. Tutton, D.Sc., F.R.S.

In this paper the results are given of the investigation of the double salts potassium-nickel selenate, rubidium-nickel selenate, cæsium-nickel selenate, and ammonium-nickel selenate, each containing six molecules of water of crystallisation. The results are absolutely in line with all those already published for the complete monoclinic double sulphate series with $6H_2O$, and for the isomorphous magnesium and zinc double selenate groups. The morphological and physical properties exhibit the progression in accordance with the atomic weight of the alkali metal which has been so clearly brought out by the previous work, and the ammonium salt is shown conclusively to belong to the isomorphous series, and to exhibit the peculiar traits described in connection with the other ammonium salts of this monoclinic series already dealt with.

Two points may, however, be emphasised. Firstly, the remarkable quantitative manner in which the law of progression is shown in the cases of the alkali metallic salts. For the average of all the changes in interfacial angles when potassium is replaced by cæsium is exactly double that for the replacement of potassium by rubidium, corresponding precisely to the change of atomic weight which is also almost exactly double (93 to 46). The angular averages are 47′ and 23′. The maximum change of angle also shows the same exact progression, the values being 1° 59′ and 57′. That the ammonium salt is really isomorphous is proved by the fact that when ammonium is introduced for potassium the average and maximum changes of angle are no more, and, indeed, just slightly less, than if cæsium were introduced, namely, 45′ and 1° 50′.

The second point worthy of emphasis is the extreme closeness of the molecular volumes and the topic axial ratios of the rubidium and ammonium salts of the group, representing the volumes and edge dimensions of the unit cells of the monoclinic space-lattices of the two crystal structures. The values indicate very perfect congruency and almost identity of the two structures. It will be shown in a separate communication immediately following this paper, that this result, forming a particularly clear example of a fact observed concerning the ammonium and rubidium salts of every group investigated by the author, has an important bearing on the theory of valency volumes, for that theory is entirely incapable of explaining it.

"*X-Ray Analysis and Topic Axes of the Alkali Sulphates and their Bearing on the Law of Valency Volumes.*" By A. E. H. Tutton, D.Sc., F.R.S.

An X-ray spectrometric analysis, carried out with the author's crystals in the laboratory of Prof. W. H. Bragg by Prof. A. Ogg and Mr. F. Lloyd Hopwood, of the rhombic crystals of the alkali sulphates R_2SO_4, where R is K. Rb, Cs, and NH_4, has indicated that four molecules of R_2SO_4 are contained in the unit rectangular cell of the space-lattice, as suggested by the author in 1894. The atoms of sulphur occupy the corners of the rectangular cell and the middle point of each side. The planes of sulphur atoms parallel to the (001) face are of pseudo hexagonal structure, the atomic centres being arranged in nearly regular hexagons, as suggested by Federov and adopted by the author. The metallic atoms are also probably arranged in nearly regular hexagons.

The X-ray measurements of the absolute lengths of the edges of the rectangular unit cells (the distance apart of the S atoms in the three rectangular directions) agree perfectly with the topic axial ratios for these salts determined by the author. A new series, based on still more refined density determinations, is now published, and the agreement leaves nothing to be desired.

A remarkable congruency (close approximation to identity) of the structures of rubidium and ammonium sulphates is indicated, the molecular volumes and topic axial ratios being very near for the two salts. The fact is not an isolated one for the simple sulphates, but has been also observed in the case of every pair of ammonium and rubidium double sulphates or selenates examined by the author. This result is fully confirmed by X-ray work on simple sulphates. The absolute volumes of the unit cells of the two salts are within 1 per cent of identity, just as are the molecular volumes, and the absolute lengths of the edges are correspondingly close, just as are the topic axial ratios.

It is thus fully substantiated that the constants, molecular volume and topic axial ratios, afford true indications of relative volume and dimensions of elementary space-lattice cells in the cases of crystal structures of isomorphous series.

As the volume of unit cell of ammonium sulphate should be at least twice that of rubidium sulphate according to the Valency-Volume Theory of Barlow and Pope (if we assume triadic valency for nitrogen, since the sums of the fundamental valencies of $(NH_4)_2SO_4$ and Rb_2SO_4 are respectively 24 and 12), and more than twice if nitrogen be pentadic (the volumes then being 28 to 12), whereas the volumes of the unit cells of the two salts are now proved by direct X-ray measurement to be nearly identical, it is obvious that the Valency-Volume Theory does not represent a law of nature. A crucial test has thus been applied, and the decision is against the theory.

"*Scattering of Plane Electric Waves by Spheres.*" By T. J. I'A. Bromwich, F.R.S.

The first section contains a very general solution of the electro-magnetic equations in curvilinear co-ordinates, and it is proved that this solution contains as particular cases those previously obtained by Hertz, Fitzgerald, Rayleigh, Love, and Lamb.

This general solution is then applied to the problem indicated in the title of the paper, and the results are analysed further in two particular cases, corresponding to long waves and to short waves. The former of these has been previously considered by Rayleigh and by Love, but some new formulæ are found here. The latter is treated first by Macdonald's method, and, secondly, by a new method which, however, seems closely related to a second process due to Macdonald. The results obtained by these two methods are found to be consistent.

The formulæ deduced here for the case of short waves have been tested numerically for the values given by $\kappa a = 9$ and 10; that is, for wave-lengths one-ninth and one-tenth of the perimeter of the sphere. The details of the comparison will be found in the paper by Messrs. Proudman, Doodson, and Kennedy, but it may be stated that the agreement is quite close except behind the sphere. Even there, the formulæ are quite satisfactory at an angular distance less than 10° from that of the incident waves.

"*Numerical Results of the Theory of the Diffraction of a Plane Electro-magnetic Wave by a Perfectly Conducting Sphere.*" By J. Proudman, A. T. Doodson, and G. Kennedy.

This paper is entirely concerned with the computation, from quoted formulæ, of the electric disturbance at a great distance from the sphere. The length of the incident wave being $2\pi/\kappa$ and the radius of the sphere being a, the results are obtained for $\kappa a = 1, 2, 9, 10$. Tables and curves are given of the results, and also of the principal stages of the work.

The methods of carrying out the computations, the means of securing accuracy and detecting errors, and an analysis of the results are also given.

At the meeting on November 30, 1916, the following Officers and Members of Council were balloted for and elected:—

President—Sir J. J. Thomson, O.M., M.A., D.Sc., LL.D.

Treasurer—Sir A. B. Kempe, M.A., D.C.L.

Secretaries—Prof. A. Schuster, Sc.D., Ph.D., and W. B. Hardy, M.A.

Foreign Secretary—Prof. W. A. Herdman, D.Sc.

Other Members of the Council—Prof. J. G. Adami, M.D., H. T. Brown, LL.D., Dugald Clerk, D.Sc., Prof. A. R. Cushny, M.D., Prof. A. Dendy, D.Sc., Prof. P. F. Frankland, LL.D., Prof. J. W. Gregory, D.Sc., H. Head, M.D., J. H. Jeans, Major H. G. Lyons, Major P. A. McMahon, D.Sc., Prof. F. W. Oliver, D.Sc., Prof. C. S. Sherrington, M.D., Prof. A. Smithells, B.Sc., Hon. R. J. Strutt, M.A., and R. Threlfall, M.A.

SOCIETY OF CHEMICAL INDUSTRY
(London Section).

Ordinary Meeting, November 20, 1916.

Mr. Arthur R. Ling in the Chair.

The Chairman, in opening the meeting, said he had to refer to the loss of two past Presidents of the Society since last they met.

Sir William Ramsay, who was their President from 1903—1904, passed away after a long and painful illness on July 23 last. He said it would ill befit him to dilate up the achievements of this distinguished man of science. His name was a household word, and his works were known to all. They had on many occasions welcomed him in that room, both in bringing before them his remarkable discoveries and in discussing various papers. To all who knew him his modest and genial personality, which was not in the least affected by the honours showered upon him, would be remembered.

Dr. David Howard, who passed away the previous week, was, he belived, one of the foundation members of the Society. He occupied the Presidential Chair in the year 1886 7. Probably no one had been closer associated with the Society and its work, as an active member of the Committees and of the Council, than Mr. David Howard, and certainly no one was better known to the members. If he belonged to the old school of chemists at least one could say that his knowledge of science was profound, and his genial manners endeared him to everyone. He would ask Mr. Tyrer, the close personal friend of Mr. Howard, to add his tribute.

Mr. Thomas Tyrer said that he had been associated with Mr. David Howard since they were students together under Hofmann at the College of Chemistry. Perhaps the distinguishing feature of Mr. Howard throughout his life had been his probity, which was reflected in the great firm to which he belonged.

The President of the Society, Dr. Chas. Carpenter, then delivered an Address to the members on "*Chemistry and Engineering.*"

He said he proposed to initiate a talk about chemists and engineers, and their relationship to the great problem of bringing up to date their national chemical industries. The Charter of the Institution of Civil Engineers defined the profession of the engineer as being the art of directing the great sources of power in Nature for the use and convenience of man. They might in similar language define the aim of the chemist as being to wrest from Nature some of her most hidden secrets for the same purpose. He attached no importance to the definition of a chemist which described him as an organic body more liable than any other of similar nature to spontaneous explosions.

The popular conception of the engineer was that he was an empiric who had been trained on cotton-waste and engine-oil. This was of course a fallacy. He had just as scientific a foundation for his work as had the organic chemist, and like him had a ring structure for the starting-point from which sprang his great creations. The engineer's ring, however, was centuries older, and it was basic in simplicity. It was formed round a triangle having rigid sides and a flexible base. If force were applied to the apex it was stable and resisted distortion; in other words, it did the work expected of it. If force were applied to either of the other two angles it was seen to be unstable and collapsed. Two such rings might be joined together with a common base, and the two rings so coupled became a structure which had similar attributes to its components. If force were applied to either of both apexes, this double ring was stable; if to the opposite angles, it was unstable. But if the two complete rings were combined to form a compound ring, the structure became a stable one in all directions. The simple ring formation thus described was the basis of allconstruction and building in metals, from the framework of a Zeppelin to that of the Forth Bridge.

The President then considered how the engineer started to work to achieve his task of construction. He must perforce have an imaginative faculty, and see in his mind's eye the general outline of his finished production before its creation was begun. Drawings or maps would be useless to him without a knowledge of the surrounding landscape itself. Referring particularly to the construction of the Forth Bridge, the President said the engineer watched the long slope of land stretching down to the river's edge from Fife on the one shore and from Linlithgow on the other, and he realised that what he built must join those lofty crests. He set up on either bank of the river a compound ring structure, placing another on the island of Inchgarvie. On these points he erected his massive compound rings, and from both sides he proceeded to build out other rings each balancing the other, and growing smaller and smaller as they stretched across the waters below, forming what was known as cantilevers.

Further, if they contemplated a modern battleship, consuming fuel at the rate of over one thousand tons of coal per day, and imagined the mechanism of the appliances capable of producing energy on such a scale down in the bottom of the ship's hold, and utilising it within her walls, no one would have any doubt as to the important part played by the engineer in such an organisation. And yet, until quite modern times, engineers were looked upon in the same more or less contemptuous fashion as they not infrequently were by chemists to-day. In recent years, however, one man great above his fellows set himself to remedy this set of things which threatened seriously to menace the efficiency of the Navy and the safety of the Empire. That man was the present Lord Fisher, and with the thoroughness born of the Service, to which from boyhood he was attached, he realised the importance of beginning early, and instead of taking youths who were more or less spoilt by the kind of training given them at the public schools, the entering age for naval cadets was made thirteen years or a little older. At that age the cadet was expected to satisfy his examiners in English, history, geography, arithmetic, geometry, French or German, with some knowledge of Latin. Then his training began in physics, chemistry, applied mechanics, applied electricity, and above all in engineering with workshop practice. Whether he was destined for a battleship commander, an engineer commander, or head of a dockyard, the value of engineering in the making of a man was first recognised from the commencement. The boy of sensitive poetic spirit, the ruminating young philosopher, the scholar whose whole heart was in his books, were types that had a real use in the world, but their proper place was not in the navy. The boy of the right sort would, within the limits natural to his age, show initiative and readiness for responsibility.

It seemed to him that the condition of affairs in the chemical industry was very much akin to what had happened in the navy, specialised engineering was becoming more and more necessary to it.

He believed it was increasingly necessary for the engineer to take a larger part not only in the design but in the running of plant in the chemical factory. He did not mean that the control should not be chemical, for he thought in the majority of cases, if not all, it must be, but he was convinced that when the conditions were found and laid down the engineer would be quite capable of carrying them out, whilst his natural ability for handling men and material could not but be most useful.

If they started with the idea that everybody could be turned out an engineer or a chemist they would go hopelessly wrong. The function of teachers should be to ascertain in what direction the mental capacity of a student lay, and to direct him to follow the right main road. If they were to maintain their position among the nations then they would have to make a radical change from pre-war methods. The engineer should be taught enough chemistry to enable him to appreciate the chemist's point of view, and the chemist should know enough of engineering to realise that with the engineer thus trained he could leave the practical application of the processes he devised in the laboratory as well as supervision in the chemical works.

Mr. G. W. MacDonald said that he was thoroughly in agreement with what the President had said, and that the success of his own firm (Messrs. Henry Tate and Sons, Ltd.) had been assured by applying the same plan which Dr. Carpenter had advocated. They had in this way been able to defy foreign competition, even though the latter had been protected.

Mr. Thomas Tyrer expressed himself in favour of co-operation between the chemist and engineer.

Prof. G. T. Morgan said that he was glad to find that in the title of the President's Address chemistry had been placed before engineering, although many engineers had characterised chemist as molecule jugglers. There had been and still were a class which he would characterise as Malthusian chemists, who thought it waste of time to produce new chemical compounds, and ignored synthetic chemistry. He could not help thinking that the reason France had lost her predominant position in chemical manufacturing was that her people had failed to recognise the important work of Kekulé. They all knew how difficult it was to visualise synthetic chemical work on the production of a dye before Kekulé's generalisations had been introduced, and at the present time there was a tendency to ignore the work of Werner in Germany, which to his mind was equally important.

Dr. H. G. Colman said that in his opinion chemical manufacturing required not only the co-operation of the chemist and engineer but also of the business man.

Mr. Hinchley put forward a plea for the creation of the chemical engineer. In support of his view, he pointed out that the chemical engineer differed from the mechanical engineer in that he must possess a knowledge of chemistry in guarding against corrosive action of certain substances on the materials of which his apparatus was constructed.

Mr. Bertram Blount said that he was a chemist who did not claim to be an engineer, and he had frequently had to collaborate with engineers who did not claim to be chemists. In his opinion what was needed was co-operation of these technologists without jealousy. He disagreed with the introduction *ad hoc* of the chemical engineer, and he thought that those who advocated the production of such an individual must really mean the ordinary experience they gained in professional work, which caused them to appreciate and sympathise with technologists in other branches of science.

Col. Smithells said that he had been told that it was necessary to produce a chemical engineer at college. In his opinion, however, this was quite an impossibility, and he agreed thoroughly with what their President had said in regard to creating a sympathy between engineers and chemists.

Prof. Donnan, whilst admitting the great value of the synthetic chemist, thought that more problems in a works were presented which necessitated those trained in physics and engineering than in pure chemistry.

Prof. Armstrong pointed out that the President was the first engineer to occupy the Presidential Chair, and that he was one of the very few engineers who had shown effective appreciation of the chemist's work. A long experience as a teacher of the two classes of students had convinced him that the chemist and the engineer were men of very different types of mind, and that the important step to be taken was to train them in such a way as to promote mutual respect and understanding.

The Chairman, in moving a vote of thanks, said that it was unusual to discuss an Address delivered by the President. He would point out, however, that the discussion had not been of a critical nature, for all the speakers had been in agreement with the President, even those who advocated the creation of a chemical engineer for what they meant was, as Mr. Blount had pointed out, sympathy between the two branches of science which could only be gained by professional experience. A man after he left college might become a chemical engineer or an engineer chemist according to his environment.

FARADAY SOCIETY.

Ordinary Meeting, November 8, 1916.

Sir Robert Hadfield, F.R.S., President, in the Chair.

A General Discussion on "Refractory Materials" was opened with an Introductory Address by the President.

In spite of the vital importance of refractories to many national industries, the subject has received little attention in this country during the last few years, and in many instances the industry had not the scientific foundation required for its healthy development. That was the justification for the present symposium, out of which it was hoped improved practice would spring. The chief sources of refractories were probably silica, chrome clay, magnesite, dolomite, chromite, bauxite, graphite, and zirconite. The President next touched on the question of the properties of refractories, and he gave an abstract of the "Standard Specifications for Refractory Materials" published by a joint Committee of the Institution of Gas Engineers and the Society of British Gas Industries in 1912. In 1908 Mr. J. F. Bywater had read an important paper on this subject before the former Institution, and this was being reprinted in connection with the present meeting. An interesting *résumé* was given here as to the origin of fireclays, and it was shown how difficult it was to establish a relation between their fusibilities and compositions based merely on ultimate analysis. "Mechanical" analysis was first necessary, and the material divided up into kaolin, or true clay substance, quartz, and felspar. Of these the first, $Al_2O_3.2SiO_2$, is the most infusible. The amount of accompanying fluxes, iron oxides, lime, magnesia, potash, and soda—which flux in the ratio of their equivalent combining weights is, however, a very important factor.

The Address next dealt with the classes of refractories in use, namely, acid, basic, and neutral, and the special properties and uses of each were indicated. The comparatively new refractory zirconite was discussed in somewhat fuller detail. A series of exhibits illustrated some differences in practice between good and bad refractories. Thus the diameter of a magnesite nozzle remained quite unaltered at 1 in. even after 28 tons of steel had been poured through it, whereas that of an ordinary fire-clay nozzle increased to 2 in. The difference might well represent slag embedded in the steel.

Some photomicrographs were shown, illustrating the use of microscopy in the study of refractories, and the Address concluded with a bibliography of papers and books and with a series of tables giving complete analyses, largely compiled from the author's own records, of most of the refractories in common use.

The opening paper of the symposium was given by Dr. J. W. Mellor (Stoke-on-Trent), and it dealt with "*The Texture of Firebricks.*"

What constitutes a good firebrick is a favourite question, and one which does not admit of a satisfactory answer. The requirements from firebricks vary so widely in different furnaces, or in particular parts of a single furnace, that the ideal firebrick can be defined only in abstract terms, and this the more because some properties can be highly accentuated only at the expense of others.

Texture is one of the most important qualities of a firebrick, since, assuming that the chemical composition and refractoriness are otherwise satisfactory, the life and character of the firebrick are largely determined by its texture. The texture of a refactory may vary from that of the light porous bodies used in making bricks for insulating boilers, &c., to non-porous or vitreous bodies used in making crucibles, acid-resisting bricks for acid towers, &c. There are quite a number of intermediate types. The different types of texture were exhibited. The samples were prepared by cutting the brick transversly, polishing an exposed face, and finally cementing a glass plate on the polished faces by means of hot Canada balsam.

It was shown that the refractoriness of a firebrick under ordinary conditions of measurement is dependent to a small extent on the grain-size. The after-contraction of firebricks and the after-expansion of silica bricks is due to the arresting of the changes which occur during the firing of a brick before they are completed.

For bricks which have to resist the abrasive action of streams of flue dust, coal ashes, slags, &c., a close texture is necessary; but a close texture brick is liable to split with abrupt variations of temperature. To reduce the tendency to splitting in this way, a uniform texture is desirable. The chemical composition of the brick in relation to that of the dust and slag it has to resist at high temperatures is of great importance. Examples illustrating the importance of both texture and chemical composition were shown. In slags which exert a severe action on the firebrick, the importance of small well-fitting joints, cemented by a good jointing clay, was also emphasised, since with bricks having a close uniform texture and the right chemical composition the joints are the weakest places.

Other examples were also given, showing that the texture of a firebrick is as important as chemical composition and refractoriness. The texture is a property which can be largely controlled by the manufacturer, whereas the other qualities are not so amenable to treatment. It was shown, by using the blast-furnace as an illustrative example, that the consumer must carefully consider the conditions which prevail in different parts of any particular furnace before he selects for trial particular types of texture as likely to suit particular parts of his furnace.

Prof. W. G. Fearnsides (Sheffield) spoke principally on "*The Application of Petrographic Methods to the Study of Refractory Materials.*"

By way of introduction Prof. Fearnsides called attention to the circumstance that, though there is a woeful lack of scientific data to help makers of refractory materials who are starting a new line to command certain success in any one of the manufacturing processes involved in the making of a brick, there is among the foremen brickmakers and furnacemen a great deal of information which only needs to be collected, codified, and interpreted to make it as scientific as the best laboratory product. One of the most pressing necessities in refractory material manufacture at the present time is for scientific workers to go through the works and listen when practical men bring out information in terms which are the language of the brickyard or the foundry, and which they should translate and express in the international language of time and inversion-temperatures of grain-sizes and chemical compositions which are the usual currency of those superior people who think they know. A great deal might also be accomplished if actual makers who have obtained a measure of success and users who are subjecting the material manufactured to unusual stress would work together and face awhile each the other's difficulties, and if, alongside, there might be a competent and sympathetic man of science who would stand by and hold the balance and occasionally give his help to spoke a wheel, the progress of the refractory-making industry would be more rapid than many people think. Though in its best developments the art of making refractory materials is in advance of the science, the practice of the art, by unskilled makers, leaves much to be desired, and it is certain that out of a scientific study of the craftsman's methods would come experience, in the light of which repetitive practice might, with advantage, be scientifieally controlled.

Referring to the application of the microscope to the study of refractory materials, Prof. Fearnsides recalled the pioneer work done by the late Henry Clifton Sorby, of Sheffield, who some fifty years ago in the course of his early work on the physical constitution, first of rocks and afterwards of metals, rubbed down preparations both from silica bricks and fire-bricks to a condition of fair transparency. In determining the texture of any brick the thin slice method is one of direct and easy application. In the study of the relationship between the plums and the porridge which together make up a brick, great skill of manipulation is required to bring the method to any great success. Attainment of a technique which will make evident the character of the "binder" has offered greater difficulties than either the slicing of rocks or the preparation of polished and etched surfaces of almost any metal. These difficulties, however, should not be insuperable, and in a brick made from basic materials in which high refractive-index is a characteristic property (*e.g.*, magnesia, chromite, shrunk-bauxite, zirconia, and the like), one knows enough already to judge at a glance the measure of success which the brick manufacturer has attained, and with experience to guide one it is not difficult to foretell approximately how particular batches of bricks will behave in the furnace. With new-made silica bricks, and especially with fire-bricks, the determination both of the composition and of the intrinsic nature is not so easy, and with slices of normal thinness (between 1/500th and 1/1000th of an inch), new formed minerals are in such tiny crystals that they generally interfere one with another and appear as a felted mass. Characteristic inversions of quartz to tridymite and crystoballite in silica bricks are comparatively easy to observe, and from structures revealed by the petrographical microscope one can determine with fair accuracy the heat treatment which a silica brick has received. More satisfactory, however, from the point of view of demonstration specimens, are micro-preparations cut from the bricks turned out from the linings of larger furnaces when those furnaces are dismantled at the termination of their run; and probably it is by careful selection and the scientific study of the more successful of these highly metamorphosed end-products that scientific workers will first gain information which may suggest a probable direction for the manufacturer's next advance.

At this point the President asked Dr. R. Lessing to show a series of specimens illustrating a method of testing he had devised five or six years ago for ascertaining the Texture and Rational Composition of Refractory Mixtures before Firing.

The method consists of a simple process of elutriation, by which the true clay substance of the "green" clay is removed by a gentle current of water and separated from the water by allowing it to settle out on standing. The rate of flow of water is so adjusted that the "grog," *i.e.*, the previously fired portion of coarse particles which eventually forms the rigid skeleton of the fire-brick, and also the heavy and coarse grain residue of the "green" clay, consisting of sand, shale, or carbonaceous substances, are left behind in the elutriating vessel.

Elutriation is continued until the last clouds of clay substance are removed and the water becomes perfectly clear, with the lightest portions of the residue floating just below the outlet.

A very simple form of elutriator, accurate enough for works purposes, consists of a tall glass cylinder into which the water is passed through a glass tube reaching nearly to the bottom. The cylinder is placed in a bucket, into which the clay suspension overflows, and to which the clear water is syphoned off after settling. For the purpose of the test about 500 grms. of the sample (which may be taken before or after "tempering" or from a moulded body before or after drying) are well soaked in water and washed into the cylinder. The resultant products of clay and residue are dried, and a grading test is then performed on the residue, from which the texture of the body and the ratio of grog, granular clay, shale, and coal can be ascertained.

The specimens exhibited showed that before the standard specification was adopted mixtures for gas retorts contained very little grog, which had, moreover, suffered largely from excessive crushing, yielding dust, whilst the "green" clay serving as binder had largely remained in the form of coarse granules, instead of being reduced to fine powder. The change in manufacturing methods, by which the "grog" is crushed and graded separately and the powdered "green" clay mixed with it, were shown by specimens taken after the adoption of the standard specification. For comparison, a sample of a German retort mixture was shown, which was remarkable for its large proportion and size of grog, viz., 66 per cent, as against about 35 per cent in English retorts, and also for the total absence of clay residue, shale, or coal, indicating that the binding clay had undergone some preliminary purification.

The test has been used successfully for the daily control of manufacturing operations, and is recommended by the author for this purpose, and in the absence of a reliable quantitative method for ascertaining the textures and rational composition of refractories is a simple and useful guide.

Dr. H. G. Colman gave a short account of the work on Refractory Materials carried out by the Joint Committee appointed on this subject by the Institution of Gas Engineers and the Society of British Gas Industries.

This Committee, consisting of representatives of both the users and manufacturers of refractory goods for gas-works purposes, had, after determination of the conditions prevailing in gas retort settings under present-day conditions, drawn up provisional specifications relating to the different classes of fire-resisting goods commonly in use in gasworks—namely, retort material, ordinary fire-bricks, and silica bricks—prescribing, among other more general matters, the physical tests with which these goods must comply. In addition the Committee were carrying out investigations on matters likely to be of value to both users and manufacturers, and to assist in the provision of the fire-resisting materials most suitable for the above purposes. The means at their disposal, however, had not enabled them as yet to make more than a commencement of the work in this respect, investigations being now in progress on points such as the effect of pressure on the refractoriness of materials, the relative effects of an oxidising and reducing atmosphere, and the influence of the fine flue dust carried into the hot setting on the life of the materials employed.

(To be continued).

MISCELLANEOUS.

Unusual Ores.—The Foote Mineral Company's latest price list contains some interesting items. Cerium-iron (Pyrophoric) for lighters is supplied in round or square section rods. Thorium and cerium nitrates, zirconium ores which are coming into use as furnace lining and in crucible manufacture, tungsten and its compounds, titanium, magnesium, &c., are listed at reasonable prices, and can be supplied in almost any quantity. The price list is published monthly, and can be obtained on application to the Foote Mineral Company, 107, North Nineteenth Street, Philadelphia.

"The Electrician" Electrical Trades' Directory and Handbook.—The "Big Blue Book" for 1917 is in course of preparation and will be issued early in the New Year. In addition to British, Colonial, and foreign electrical industries and manufactures, useful technical and commercial tables are given relating to lighting, power transmission, telegraph, telephone, wireless telegraphy, British and foreign government departments, &c. Also a Biographical Section giving particulars of the careers of eminent men connected with electricity and its applications. Subscription price 10s. 6d. net. If ordered after January 31 the price will be 15s. *The Electrician* Office, Salisbury Court, Fleet Street, London, E.C.

MEETINGS FOR THE WEEK.

Monday, 11th.—Royal Society of Arts, 5. (Howard Lecture). "Coal and its Economic Utilisation," by J. S. S. Brame.

Wednesday, 13th.—Royal Society of Arts, 4.30. "The Development of Imperial Resources," by H. W. Fox.

Thursday, 14th.—Royal Society of Arts, 4.30. "The World's Cotton Supply and India's Share in it," by J. A. Todd.

THE CHEMICAL NEWS

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MONAZITE, THORIUM, AND MESOTHORIUM.*

By KARL L. KITHIL.

(Concluded from p. 278).

Method for the Determination of Thorium in Monazite.

Many methods of determining thorium in monazite have been described. Only the following well-known method is alone given here. (See F. J. Metzger, "A New Separation of Thorium from Cerium, Lanthanum, and Didymium, and its Application to the Analysis of Monazite," *Journ. Am. Chem. Soc.*, 1902, xxiv., 901; see also S. I. Levy, "The Rare Earths," London, 1915, p. 285).

About 1 grm. of the monazite is ground to an impalpable powder, weighed into a platinum vessel, covered with 15 to 20 cc. of concentrated sulphuric acid, and evaporated until fumes are no longer driven off. More sulphuric acid is added and heated as before. The operation is repeated several times until the conversion of the phosphates into sulphates is complete. The mass resulting is added in small quantities to about 700 cc. of water at 0° C., with constant stirring, care being used not to allow the temperature to rise higher than 2° C. The solution is allowed to stand ten to twelve hours, when it is filtered and washed. The filtrate is then nearly neutralised with dilute ammonia, 50 cc. of a cold saturated solution of oxalic acid is added with constant stirring, and the solution is allowed to stand for twelve hours. The solution is then filtered and the precipitate washed well with water. The precipitated oxalates are then washed into a beaker and treated with a strong solution of caustic potash, heated to boiling, diluted, and filtered.

The hydroxides are washed thoroughly with water and dissolved off the filter with hot dilute hydrochloric acid (1 : 1). The solution is evaporated to dryness to free it from acid, taken up with 75 to 100 cc. of water, 15 cc. of a saturated solution of sodium thiosulphate is added, and the solution is heated to boiling. It is then filtered and the precipitate and the filter set aside for subsequent filtration. An excess of ammonia is added to the filtrate, the precipitate is filtered off, washed, dissolved in hydrochloric acid, and evaporated to dryness, the residue being taken up in water and re-precipitated with thiosulphate as before. The solution is filtered through the filter-paper carrying the first precipitate, and the filtrate is treated as before. The precipitations are continued as long as the precipitate forms with the thiosulphate, three precipitations usually being sufficient to completely extrsct the thorium. The combined precipitates of thorium-thiosulphate are washed completely, dried, and ignited. The ignited mass is fused for some time with potassium bisulphate, taken up in water, and a few drops of hydrochloric acid added, and precipitated with oxalic acid. The oxalates are converted into the hydroxides, dissolved in hydrochloric acid, evaporated to dryness, taken up in water, and re-precipitated with sodium thiosulphate, filtered, washed, dried, ignited, and weighed as ThO_2.

Treatment of Monazite for the Extraction of Thorium.

Soddy gives in a short form the technical treatment of the monazite sand as it is carried on to-day in the industry. ("The Chemistry of the Radio-elements," 1911, p. 64; see also, Richard Bohm, "Die Darstellung der Seltenen Erden," Leipzig, 1905, ii., 94; S. I. Levy, "The Rare Earths," 1915, p. 276).

In the first stage of the technical treatment of the monazite sand, which is ground up very fine, it is heated with twice its weight of sulphuric acid. The further procedure in the treatment is described by Soddy as follows:—

"The cold mass is dissolved in water and left to settle. The solution is then fractionally precipitated with magnesia, the thorium being concentrated mainly in the first fractions precipitated. The commonest and most useful reagent for precipitating the rare earths from a solution containing common earths, such as alumina, iron, &c., is oxalic acid. Now thorium oxalate is of all the rare-earth oxalates the least soluble in acids, so that by working in fairly strong nitric acid solution thorium oxalate may often be precipitated and separated at least partially from the other rare earths and from calcium. The same is true of the rare-earth phosphates, that of thorium being one of the most insoluble in dilute acids. On the same principle thorium is often precipitated by weak bases, such as the substituted ammonias, for example, dimethylamine, while zirconium, &c., remain dissolved. The potassium salt of hydrazoic acid, KN_3, precipitates thorium hydroxide only from mixtures of thorium and cerium on boiling. The same separation may be effected by means of sodium thiosulphate on boiling, thorium alone being separated as hydroxide. This ready hydrolysis of weak thorium is characteristic of the element. The oxalates of thorium and zirconium alone of the rare earths are soluble in ammonium oxalate, and on strongly acidifying the solution the former alone is re-precipitated. The solution of the oxalate of thorium and its conversion into soluble salts may be effected by means of concentrated ammonium or sodium carbonate and precipitation of the concentrated solution as thorium hydroxide with strong ammonium or sodium hydrate. Thorium is distinguished from the yttrium group of the rare earths by its power of forming a double sulphate with potassium sulphate, insoluble in excess of the latter reagent, and so may be separated from a mixture of the sulphates by saturating the solution with potassium sulphate. Alike in the old, now obsolete, as in the present, technical methods of purifying thorium, the peculiar solubility relations of thorium sulphate in water have been largely applied. The older method consisted in volatilising the excess of sulphuric acid from the material being treated, and in dissolving the anhydrous sulphates in ice-cold water—a tedious operation—and in heating the solution till the hydrated thorium sulphate was precipitated. The latter was then dehydrated at 300—400° and the process repeated. In present practice the sulphuric acid is always kept in great excess in the initial treatment of the mineral, but the sulphate method may be employed at the final stage of manufacture as follows:—The thorium hydroxide is dissolved in hydrochloric acid, so that the solution contains not more than 30 per cent ThO_2, and sulphuric acid is added to the extent of 0·5 per cent more than the equivalent quantity, the temperature being kept low, and in any case below 40° as a maximum. Under these conditions the hydrate $Th(SO_4)_2,8H_3O$ is precipitated, departure from the conditions causing the separation of the tetrahydrate, which is in every way less easily manipulated. The precipitated sulnbate is re-converted into hydroxide, and the process repeated as often as necessary to remove all impurities.

"Thorium forms a curious compound with acetyl acetone, $Th(C_5H_7O_2)_4$, which is soluble in chloroform and alcohol, and can be distilled in a vacuum, and so can advantageously be employed for the purification and separation of the element.

"It may be mentioned that in the fusion of refractory minerals, as with sodium carbonate, the thorium, if present, is converted into the highly insoluble oxide, ThO_2, and its presence is apt to be overlooked.

"Thanks largely to the thorium industry, in which a product unusually pure is essential, there exist therefore a great variety of exceedingly good and sharp methods for the separation and purification of thorium, and it must be understood that ionium, if present, and radio-thorium always remain unseparated from thorium in these processes as far as they have been examined."

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* *Technical Paper* 110, U.S. Department of the Interior, Bureau of Mines.

In the manufacture of thorium nitrate from monazite a large amount of residues of the cerium group of rare earths is obtained. Monazite contains 60 to 70 per cent of the cerium group or other rare earths besides thorium, and 3000 tons—which is the annual consumption of monazite—gives about 1000 tons of cerium and about 1200 tons of a mixture of the rare earths—lanthanum, neodymium, and praseodymium oxides. Considerable research work has been done in order to utilise these waste materials, and experiments have been made with almost every one of them. In order to obtain and separate the rare-earth elements, thousands of crystallisations and fractionations are necessary, although cerium itself is separated with comparative ease. The untiring work carried on in the research laboratories of the industries, as well as by the scientists in both America and in Europe, will, no doubt, in time be crowned with successful technical applications of the by-products.

SEPARATION OF MESOTHORIUM ON A COMMERCIAL SCALE.

Monazite sand is the main source of mesothorium, and contains also uranium and, consequently, radium. Mesothorium has properties similar to radium, and the radium therefore is separated together with the mesothorium. The methods employed in the extraction of mesothorium are well known, and have been described by Haitinger and Ulrich ("Bericht über die Bearbeitung der Pechblende Rückstände," *Ber. K. Akad. Wis.*, 1908, cxvii., 619), and have been used in the extraction of radium (Moore and Kithill, "A Preliminary Report on Uranium, Radium, and Vanadium," *Bull.* 70, p. 79, Bureau of Mines, 1914).

Some manufacturers of mesothorium add a small quantity of barium sulphate to the monazite sand during its treatment with sulphuric acid, whereby the mesothorium is separated with the insoluble material left after the treatment of the product with water.

The half-value period, or period of half life (the time required in which one-half of any given quantity of radioactive matter disintegrates — becomes transformed—is called half-value period or period of half life) of mesothorium is 5·5 years, whereas that of radium is about two thousand years.

The manufacture of mesothorium alone from monazite is not profitable, as the value of the mesothorium extracted would not pay for the cost of the monazite. As a by-product from thorium nitrate manufacture such manufacture should be of importance.

QUANTITATIVE DETERMINATION OF MESOTHORIUM.

The quantitative determination of mesothorium is carried on in the same manner as for radium (Soddy, "The Chemistry of the Radio-elements," 1911, p. 46; Rutherford, "Radio active Substances and their Radiations," 1913, p. 550).

The content of mesothorium in preparations, all of which carry about 25 per cent of radium, is expressed in terms of the γ ray activity of radium in equilibrium. For example, 5 mgrms. of mesothorium on this standard indicates that the γ-ray activity of the mesothorium plus the radium contained in it one month after separation gives a γ-ray activity equal to that of 5 mgrms. of pure radium bromide.

If both the radium and the mesothorium are to be determined, then radium plus mesothorium is determined by means of the γ-ray method, and afterwards, by the emanation method, the radium alone is determined.

By the γ-ray method alone can be determined the ratio of radium to mesothorium by measuring the γ-rays before and after boiling the solutions. The content of mesothorium plus radium is found before the solution is boiled; after it has been boiled, the content of mesothorium alone is given, as the radium emanation is removed by boiling, and radium C_1, which emits the γ-rays, is, for all practical purposes, disintegrated after three hours' time.

In regard to the method of measuring mesothorium and radium by the γ-ray method, reference is made to the work of Ebler ("Chemiker Kalender" for 1914, ii., 371), and of Meyer and Hess ("γ-Strahlenmessung von Mesothorpräparaten," *Mitt. Inst. Radiumforschung*, Vienna, July 2, 1914, p. 1443).

The quantities of mesothorium that can be extracted from monazite are of course very small. One hundred metric tons of monazite, with a content of 5 per cent ThO_2, contains approximately 4·3 tons of thorium metal. According to Rutherford ("Radio-active Substances and their Radiations," 1913, p. 552), one metric ton of thorium metal contains 0·42 mgrm. of mesothorium. We have, therefore, 0·42 mgrm. of mesothorium per weight of 10^{-6} grms. of thorium, or 4·3 times 0·42 equals 1·8 mgrms. of mesothorium by weight. The activity due to mesothorium is three times as great as that due to radium when compared weight with weight. The mesothorium obtained from one ton of monazite therefore would be calculated as 5·4 mgrms. Lorenzen (private communication received from Julius Lorenzen, Tegel-Berlin, on "Chemical Manufacture of Mesothorium"), however, states that technically 2·5 mgrms. of mesothorium can be obtained from 1 metric ton of monazite, or 100 tons of monazite would yield 250 mgrms. of mesothorium. It seems, therefore, that technically a recovery of about 50 per cent is made. Mesothorium is sold on the basis of its activity compared with radium bromide of highest purity (determined by the γ-ray method), and has been sold with increasing demand at 45 to 60 dols. per mgrm. The separation of mesothorium has been widely discussed in scientific and technical papers, and is outlined above.

The manufacture of thorium nitrate from monazite is well known and has been described extensively. This manufacture, however, is briefly described above. The manufacture of the thorium nitrate is so highly developed that a recovery of 90 to 95 per cent of the thorium contained in the monazite has been made by many industrial concerns.

TABLE I.—*Minerals contained in Monazite Sands, arranged according to Specific Gravity.*

Mineral.	Specific gravity.	Letter showing relative quantitative occurrence.(*a*)
Quartz	2·65	*a*
Felspar	2·5 to 2·7	*e*
Tourmaline	3·0 „ 3·2	*g*
Apatite	3·2 „ 3·25	
Epidote	3·2 „ 3·5	
Olivine	3·3 „ 3·6	
Garnet	3·8 „ 4·3	*c*
Rutile	4·a „ 4·25	*h*
Zircon	4·5 „ 4·7	*i*
Ilmenite	4·5 „ 5	*b*
Monazite	4·8 „ 5·3	*f*
Magnetite	5·16 „ 5·18	*d*
Gold	15 „ 19	*k*

(*a*) The order varies according to localities.

Although in former years monazite and thorium nitrate were imported into this country, lately – since the manufacture of mesothorium from the thorium residues has been begun—Europe prefers to export the ash of the broken incandescent mantles, which are high in ThO_2, and keeps the monazite in order to obtain the mesothorium from the residues. The import duty on the ash brought into the United States is only 10 per cent *ad valorem*, whereas thorium nitrate pays 25 per cent duty. The thoria ash has been sold for 25 marks (6 dols.) per kilogrm. in Europe.

Minerals in Monazite Sands.

The minerals contained in monazite sands, arranged according to their specific gravity, are shown in Table I.

The conglomerate must be freed from the larger gravels and from the clays.

Proper sizing is important before concentration; in sizing the remaining clay and mica particles should be removed by a sliming process.

Four or five sizes should be made through sieves of 20, 50, 80, and 100 mesh.

Such properly sized material, when treated on the large type of Wetherill electro-magnetic separator, having two magnets and 18-inch belt, gives the results shown in Table II.

Table II.—*Results of Action of Wetherill Electro-magnetic Separator on Properly Sized Monazite Sands.*

Mineral.(*a*)	Point in separator at which mineral separated.	Current.
Magnetite	—	Very weak.
Ilmenite	First pole, first magnet; distance between poles, about 8 mm.	1 to 5 ampères.
Hematite		
Garnet..	Second pole, first magnet; distance between poles, about 3 mm.	
Platinum (if any)		
Epidote		
Apatite		
Olivine		
Tourmaline . ..		
Monazite (92 to 95 per cent) and traces of zircon and rutile	First and second pole of second magnet; distance, first pole, 6 mm.; second pole, 2 to 3 mm.	12 to 15 ampères.
Platinum, &c. (if any)		

(*a*) Residues off belt were quartz, felspar, gold, zircon, rutile, &c.

NOTE ON THE OXY-AMMONIA FLAME.

By D. L. HAMMICK.

The fact that ammonia gas will interact with oxygen, producing a flame, has long been known. Thus Hofmann *Ann.*, 1860, cxv., 285) describes a lecture experiment in which a stream of oxygen charged with ammonia is burnt at a jet. Hofmann's experiment was modified by Heintz (*Ann.*, 1864, cxxx., 102), who introduced oxygen, saturated with ammonia by bubbling through a strong aqueous solution, into the interior of a Bunsen gas flame. On turning off the supply of coal-gas the ammonia continued to burn.

Kraut (*Ann.*, 1865, cxxxvi., 69; see also *Ber.*, 1887, xx., 1113) made use of the catalytic effect of platinum and palladium to ignite a mixture of ammonia and oxygen. He succeeded in getting oxygen to burn beneath the surface of a strong ammonia solution.

Lupton (Chemical News, 1878, xxxvii., 227) describes experiments very similar to Kraut's, and, like the latter, used a platinum spiral to ignite his oxy-ammonia mixtures.

Hodgkinson and Lowndes (Chemical News, 1888, lviii., 27) used a platinum jet to introduce oxygen into a flask containing strong ammonia solution. The jet was fixed about 1 cm. from the liquid surface, and the mixture issuing from the neck of the flask ignited, whereupon the oxygen burnt at the jet. They found that at certain pressures fumes of ammonium nitrite and nitrate were produced, as might be expected from the fact of the platinum jet.

The writer has found that an oxy-ammonia flame can readily be produced by leading ammonia and oxygen into the appropriate inlets of any ordinary blowpipe burner and igniting the mixture that comes from the jet. With a small oxygen supply the characteristic "peach-coloured" flame is obtained. On increasing the pressure of oxygen a livid white central cone, surrounded by an outer sheath of pale "peach-coloured" luminescence, is produced.

As well as ordinary brass blowpipes, jets contrived of nickel and of silica were used. The oxy-ammonia flame was allowed to play on a water surface or on ice. In all cases nitrate and nitrite were readily detected in solution. In no case was the presence of hydrogen peroxide indicated.

It would thus appear that the reaction between oxygen and ammonia, that is so prominent in the presence of platinum and similar metals, occurs also to some extent when metals are entirely absent.

It may be noted that some text-books (*e.g.*, Roscoe and Schorlemmer, Shenstone, &c.) either state or imply that nitric acid is produced in the oxy-ammonia flame. No references to experiments are given, however, and seeing that, as far as the writer has been able to ascertain, Hodgkinson and Lownde's paper (*loc. cit.*) contains the only reference in the literature to the production of nitrates and nitrites in the flame, it would seem that the text-book statements rest solely on experiments with the oxy-ammonia flame in the presence of platinum.

Chemical Laboratory, Gresham's School, Holt.

ON THE
SEPARATION OF CÆSIUM AND RUBIDIUM BY THE FRACTIONAL CRYSTALLISATION OF THE ALUMINIUM AND IRON ALUMS AND ITS APPLICATION TO THE EXTRACTION OF THESE ELEMENTS FROM THEIR MINERAL SOURCES.

By PHILIP E. BROWNING and S. R. SPENCER.

Robinson and Hutchins (*Am. Chem. Journ.*, vi., 74) have recommended the crystallisation of the aluminium alums for the separation of cæsium and rubidium from potassium and lithium in lepidolite after the decomposition of that mineral by fluorspar and sulphuric acid. They have also called attention to the difference in solubility between the cæsium and the rubidium alums (see Note), and have suggested fractional crystallisation for the separation of these elements. The marked difference in solubility between the potassium alum and the alums of cæsium and rubidium makes the method quite satisfactory for the separation of potassium from these rare alkalis, but the difference in solubility between the alums of cæsium and rubidium is not sufficiently great to bring about a rapid separation of these elements.

(Note.—100 parts of water at 15—17° C. will dissolve 0·62 parts of cæsium alum, 2·3 parts of rubidium, and 13·5 parts of potassium alum).

The work to be described was undertaken to obtain some definite information as to the value of the process of fractional crystallisation when applied to the problem of separating the alkalis. The process may be briefly described as follows:—

A solution obtained from the decomposition of lepidolite by heating with fluorspar and sulphuric acid after the removal of the calcium sulphate was evaporated until on standing the mixed alums crystallised out. The mother-liquor was poured off into a second flask, and this liquid was evaporated until another crop of crystals was obtained, and the new mother-liquor poured into a third flask, and so on. The crystals in the first flask were dissolved in a small amount of water by warming, and again allowed to crystallise, the supernatant liquid being poured into the second flask upon the crystals which had formed there;

these crystals, in turn, were dissolved in this liquid, and allowed to recrystallise, and the process was continued through all the series of flasks. The crystals separating in flask number one were repeatedly dissolved in fresh water and allowed to recrystallise in this way, and the mother-liquor was kept moving along the series of flasks in succession.

By this method the more insoluble alum was concentrated at the upper end of the series, while the more soluble alum moved toward the lower end.

After six such crystallisations applied to a solution of the alkalis from lepidolite, the crystals in the first flask showed only cæsium and rubidium when examined before the spectroscope on a platinum wire, and the crystals in the sixth flask gave a decided test for potassium and a very strong test for lithium and showed only traces of cæsium and rubidium.

A mixture of cæsium and rubidium alums obtained by the above process was subjected to this same crystallisation method. After about seven crystallisations, the crystals in the first flask were found to be pure cæsium alum, but the crystals in the sixth flask, while strong in rubidium, still gave evidence of the presence of cæsium. The process of crystallisation was continued until 22 fractions had been obtained before the cæsium had been completely removed. The crystals in the twenty second flask proved to be pure rubidium alum, no evidence of the presence of cæsium being found.

Locke (*Am. Chem. Journ.*, xxvi., 166), in studying the properties of the alums, has called attention to the differing solubilities of these interesting compounds, and notes in particular the great difference of solubility of the cæsium and rubidium and iron alums (see Note) as compared to that of the corresponding aluminium alums, and it has been suggested that this difference might be of analytical value.

(Note.—100 parts of water at 25° C. dissolve 2·7 parts of cæsium alum and about 17 parts of rubidium alum).

In order to investigate this point a mixture of cæsium and rubidium iron alums was prepared and subjected to the same process described above. After four crystallisations, the crystals in flask number one gave no test for rubidium, but showed abundance of cæsium, and after the process had been continued until 8 fractions were obtained, the eighth fraction was found to be free from cæsium and contained pure rubidium alum.

A further experiment was made as follows:—Ten grms. of the mixed cæsium and rubidium alums from lepidolite were dissolved in water, and the aluminium hydroxide was precipitated by ammonium hydroxide and filtered off. The filtrate, evaporated to about 130 cc., was poured upon some crystals of ammonium ferric alum in quantity somewhat in excess of the amount necessary to allow the replacement of the ammonium by the cæsium and rubidium. The solution was then warmed until the crystals were dissolved. On cooling, crystals separated which, when examined, gave abundant evidence of cæsium but no test for rubidium.

This experiment suggested a convenient method for the formation of cæsium alum, and also seemed to show that the more insoluble alums were readily thrown out of solution by treatment with strong solutions of the more soluble alums.

This method was applied quite successfully to the extraction of cæsium from pollucite as follows:—

The mineral was decomposed by hydrochloric acid, and after evaporation and the removal of silica the acid extract was poured upon crystals of ammonium aluminium alum and warmed until the crystals had dissolved. On cooling, cæsium alum separated in abundance, and the mother-liquor, although not free from cæsium, after one treatment consisted mainly of ammonium chloride. After about two recrystallisations the crystals obtained in the first treatment were found to give no test for either ammonium or chlorine and to be pure cæsium alum. The remainder of the cæsium was easily obtained by a few crystallisations of the mother-liquor.

This method has advantages over the other methods for the extraction of cæsium from pollucite which involve the precipitation of the cæsium as the double lead or antimony chloride, and the decomposition of these compositions by hydrogen sulphide or ammonium hydroxide.

A few experiments were made to determine the insolubility of the cæsium and rubidium in a saturated solution of ammonium aluminium alum. It was found that 1 cc. of a solution of $RbCl$ containing 0·0002 grm. Rb would give a perceptible precipitate when treated with 5 cc. of a saturated solution of ammonium alum, and that 1 cc. of a solution of $CsCl$ containing 0·00005 grm. Cs would give a precipitate of cæsium alum.

By the careful study of conditions and the use of the other alums it is hoped that these observations may lead to some advances in the analytical study of these elements, and we hope to give further attention to this problem.—*American Journal of Science*, xlii., 279.

FUEL ECONOMY.*

Introduction.

The national aspects of fuel economy may be considered from two somewhat different standpoints, namely, (1) in view of the economic situation created by the war, which will necessitate the general adoption of more scientific methods in the future development and utilisation of the nation's mineral reserves, and (2) in view of that remoter, but possibly not far distant, future when our available coal supplies will be restricted by approaching exhaustion. In approaching its task the Committee decided that it could best serve the national interest by concentrating its attention upon the more immediate aspect af the problem.

It can hardly be questioned that the chief material basis of the great industrial and commercial expansion of this country during the past century has been its abundant supplies of easily obtainable coal, which, until recent years, has given us a position of advantage over all other countries. It is also equally true that we can no longer claim any advantage in this respect over our two closest competitors.

There can be little doubt but that up to the present we have been wasteful and improvident in regard to our methods of getting and utilising coal, and that not only are great economies in both these directions attainable, but also that the question of the general adoption of more scientific methods in regard to these matters is one of vital importance, in view of the trying period of economic recuperation which will immediately succeed the war.

For some years before the war the average price of coal at the pit-head had been decidedly on the up-grade, owing chiefly to deeper workings, higher wages, and greater precautions for ensuring the safety of the mines. The result of the great coal strike of 1912, and the legislation which it provoked, was to accentuate this tendency. And if, as seems probable, prices continue to rise for some time after the war at an accelerated rate, as compared with the pre-war period, the question of the best utilisation of fuels will be of increasing importance to the nation.

If anything ought to arouse public opinion to the gravity of the situation, it is surely afforded by the statistics published in the Report upon the World's Coal Resources, issued by the International Geological Congress in the year 1913. According to this estimate, the geographical distribution of the world's total possible and probable reserves of coal of all kinds available within 6000 feet of the surface (amounting in all to 7,397,553 million metric tons) may be represented diagrammatically (Figs. 1 and 2).

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* First Report of the Committee (Prof. W. A. Bone, Chairman Mr. E. D. Simon, Secretary). Read before the British Association (Section B), Newcastle Meeting, 1916.

Percentages of World's Total Coal Reserves.

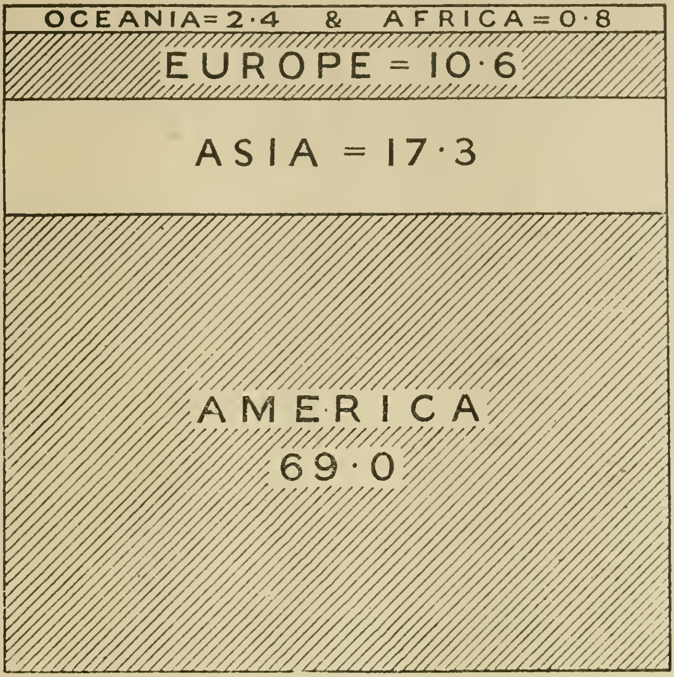

Fig. 1.

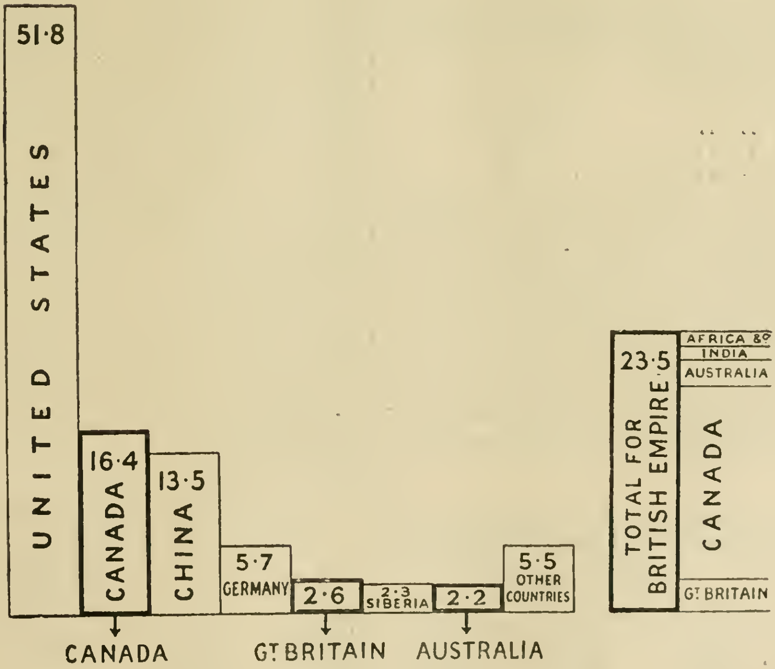

Fig. 2.

The fact that the available reserves of coal in Great Britain only amount to about one-fortieth, whilst those of the whole Empire do not amount to more than about one-fourth of the world's estimated total, is one which ought to be brought home to everyone responsible for the economic development of our national and imperial resources, especially in view of the fact that the United States, whose competition in the immediate future will probably be much more severely felt than ever before, possesses more than half the estimated world's coal, and that also in regard to the two prime considerations of quality and cost of production she probably compares favourably with Great Britain and the Empire.

Moreover, it may be pointed out that in the United States both the Government and the University of Illinois have, for some years past, conducted numerous important chemical investigations and large-scale trials upon the character of the principal American coal seams and their adaptation for various economic ends, and that, in consequence, American manufacturers have at their disposal much more complete and systematic information about their country's coal resources than is at present possessed by their British competitors. Also, the United States Government, which is continually extending its policy of the conservation of its natural resources, has already taken legislative steps to prevent the premature exploitation of the coalfields of Alaska. Nor has Canada lagged behind her neighbour, as is proved by the recent exhaustive "Investigation of the Coals of Canada with Reference to their Economic Qualities," conducted at the McGill University, Montreal under the authority of the Dominion Government, and published in the years 1912 and 1913 by the Department of Mines in six imposing volumes. No such comprehensive investigations have ever been undertaken in this country, where they are much needed. The Committee is of opinion that the example of the United States and Canada might be followed with advantage to the industrial community by the Government of Great Britain, and that representations should be made with the object of inducing the Government to provide adequate funds in aid of further researches and investigations upon the chemical character of the principal British coal seams, the best means for their future development in the national interest, and upon problems of fuel economy, including the utilisation of all the by-products obtainable from coal.

The rapid increase during recent years in the world's demands for coal is shown by the following aprroximate figures covering the ten year's period immediately preceding the outbreak of war:—

Year.	Approximate total millions of tons.
1903	800
1908	1000
1913	1250

From these figures it would appear that, during the period in question, the world's demands have continuously increased at a compound interest rate of nearly 5 per cent per annum. Another important fact is that these demands have been principally met by three countries, namely, the United States, Great Britain, and Germany, which, between them, have hitherto annually raised 83 per cent of the total anthracite and bituminous coals consumed in the world. This being so, it is of interest to compare the relative rates of increase in the coal productions of these three countries during recent years, which may best be deduced from a comparison of quinquennial averages over a period of fifteen years, from 1900–1914 inclusive (Table I.).

Table I.—*Coal Productions of the United States, Great Britain, and Germany—Quinquennial Averages* 1900 *to* 1914.

Period.	Millions of tons per annum.		
	United States.	Great Britain.	Germany (*a*).
1900—04 ..	288·2	226·8	112·5
1905—09 ..	400·5	256·0	139·8
1910–14 ..	519·2	269·9	168·3

(*a*) Excluding lignites and brown coals.

From these figures it may be inferred that up to the outbreak of the war the coal output of the United States was increasing annually at a compound interest rate of about 6 per cent, that of Germany at a componnd rate of about 4 per cent, whilst the British output was increasing at a compound rate of 2 per cent only. During the period 1910–14 the United States produced nearly twice as much coal as Great Britain, and, assuming that these relative rates of increase are maintained after the war, it may be predicted that Germany's output of coal will overtake that of Great Britain about twenty years hence, when each country will be producing some 420,000,000 tons per annum.

The public cannot be too often reminded that not only is coal of prime importance as a fuel, but also that, when suitably handled by the chemist, it yields very valuable by-products, which are the raw materials of important industries. Thus from coal-tar, and other by-products of its distillation, are obtained the raw materials for the manufacture of both synthetic dyes and drugs, and certain high explosives. Another important by-product obtainable is ammonia in the form of sulphate, which is chiefly used as a fertiliser in the production of foodstuffs. The use of artificial fertilisers, including ammonium sulphate, by agriculturists in Great Britain is still in its infancy, and the near future ought to see a large expansion in the home demands for nitrogenous fertilisers.

Among other products obtainable by the low-temperature distillation of coal are liquid hydrocarbons of the paraffin and naphthene series, and it is probable that large quantities of "motor spirit" could be manufactured in this country from coal. There is no doubt that we in this country have not been sufficiently alive to the importance of recovering such by-products from the raw coal raised in our mines, and that we have been very much behind Germany in this respect. Thus, for example, whilst in the coking industry modern by-product recovery plants had been universally installed years ago throughout Germany, we were, in 1913, still carbonising about six and a-half million tons of coal annually for metallurgical coke in old-fashioned bee-hive ovens. Also, whereas our total production of ammonium sulphate from coal was in 1913 about 318,000 tons, Germany produced nearly half a million tons from a very much smaller output of coal.

The community needs to be reminded that, at least so far as this country is concerned, progress in fuel economy involves something more than increased thermal efficiency in respect of power production and of heating operations generally, important as these undoubtedly are. It also involves the whole question of the better utilisation of our coal, including the recovery of by-products and the consequent abolition of the smoke nuisance, which at present, directly and indirectly, costs the country many millions of pounds per annum.

There are two outstanding features in the history of the British coal trade to which the Committee desires to draw attention. One is the remarkably steady increase in the total output of our mines, which, since 1870, has been maintained at an almost uniform compound interest rate of 2 per cent per annum, as the table of quinquennial averages over a period of forty-five years—1870 to 1914—shows (Table II.).

Table II.—*Coal Production in Great Britain Quinquennial Averages*, 1870 *to* 1914—*Millions of Tons per Annum.*

Period.	Average output.	Calculated at 2 per cent compound interest.	Proportion of total output exported.
1870—74	121·5	121·5	0·13
1875—79	133·6	131·1	0·146
1880—84	156·4	148·1	0·172
1885—89	165·2	163·5	0·200
1890—94	180·3	180·5	0·220
1895—99	202·0	199·3	0·237
1900—04	226·8	220·1	0·27
1905—09	256·0	243·0	0·31
1910—14	269·9	268·2	0·326

British Output of Coal 1870—1914.

The second feature is the phenomenal growth of our export trade, which, during the past sixty years, has increased something like twenty-fold, both as regards the quantities and the values of coal exported. Moreover, its value relative to other values exported has, during the same period, increased fourfold, until at the outbreak of war it constituted about 10 per cent of our total exported values. We were then actually transacting over 70 per cent of the total sea-borne coal trade of the world. It must, however, be borne in mind that a considerable proportion of the exported coal supplies the needs of our mercantile marine.

Another circumstance which demands attention is the fact that the proportion of the coal raised annually in the United Kingdom which is exported has been doubled within the past thirty-five years, trebled within half a century, and is still increasing. Three factors have operated in producing this result. One is the proximity of the finest coalfields to our ports, another is the increased demands for coal from Europe and South America, while a third has been the phenomenal growth of our mercantile marine.

The foregoing figures for the total outputs of our mines by no means represent the real rate of depletion of our available coal reserves. A vast amount of usable coal is left behind in the mine because, under present individualistic conditions, it does not pay to bring it to the surface. A larger profit on the capital of a colliery company can often be earned by working the better classes of coal and leaving the less valuable grades underground. According to figures issued in the Report of the 1905 Royal Commission on Coal Supplies, this wastage amounted to nearly 25 per cent of the total raised in the larger coalfields. The question of checking this wastage by finding out in what ways the less valuable grades can be turned to good account commercially is one of supreme national importance, and the Committee desires to draw special attention to it. Much of the coal now left behind in the mines ought to be converted into useful forms of energy and products for public purposes, and one of the most important aspects of the fuel economy problem in Great Britain is the devising and organising of means for making it possible to raise this hitherto wasted coal at an economic advantage.

So much for the general statistics of coal production. Coming now to the possible saving in the coal consumed annually in this country at the outbreak of the war (nearly 200,000,000 tons), it will be remembered that the 1905 Royal Commission on Coal Supplies found that the possible saving in our then annual coal consumption (167,000,000 tons) amounted to between forty and sixty million tons. There are many competent judges who consider that, notwithstanding the improved apparatus which has been put into use in the best factories throughout the country during the last ten years, the average result obtained for the country as a whole still lags behind the best obtainable to-day in as great a proportion as it did in 1905. It will be the business of this Committee (1) to estimate as nearly as may be the present possible margin of saving, and (2) to point out the particular directions in which it can be attained from a national point of view.

Organisation of the Committee's Work.

Having regard to the magnitude of its work, and the fact that the coal question is one upon which almost every branch of manufacturing and transport industry is dependent, the original Committee of thirteen members appointed by the Association in October, 1915, decided to exercise somewhat freely its powers of co-option, so as to make a General Committee sufficiently large and representative of all the important interests involved.

For the more detailed and special study of particular aspects of the fuel question the enlarged General Committee resolved itself into the following five Sub-Committees, each of which subsequently elected its own Chairman, and, subject to its reporting from time to time to the General Commitee, proceeded to make such arrangements as seemed best for the prosecution of its work:—

(A) Chemical and Statistical.
(B) Carbonisation.
(C) Metallurgical, Ceramic, and Refractory Materials.
(D) Power and Steam Raising.
(E) Domestic Heating and Smoke Prevention.

The General Committee next appointed an Executive Committee, composed of the Chairman and Secretary of the General Committee, the Chairman of each Sub-Committee (*ex officio*), and twelve other members, which could meet frequently in London for the discussion of matters relative to the organisation and co-ordination of the work of the Committee as a whole, to deal with matters arising out of the proceedings of the Sub-Committees which might require immediate action or decision, and to receive and consider communications either from Government Departments or Technical Associations concerning subjects under investigation by the Committee.

The General Committee has met in London four times since its appointment in October, 1915, the various Sub-Committees have each met about four times since their formation in January, 1916, whilst the Executive Committee has met regularly on alternate Fridays since April 28 last. In all, thirty meetings have been held during the year.

At the first meeting of the General Committee it was decided to organise a series of conferences of manufacturers and others interested in the fuel question in a number of the larger industrial centres, for the purposes of arousing interest in the work of the Committee, of inviting co-operation and suggestions from large users of fuel, and of educating public opinion in respect of the national importance of the question.

Six conferences have already been held (as detailed in Table III.).

TABLE III.

Date.	Place.	Under the auspices of—
1915.		
Nov. 19	Stoke-on-Trent	English Ceramic Society. North Staffs Mining Institute
1916.		
March 6	London	London Section of he Society of Chemical Industry.
March 13	Middlesbrough	Cleveland Institution of Engineers.
March 29	Nottingham ..	Nottingham Section of Society of Chemical dustry.
April 5	Manchester ..	Manchester Section Society of Chemical dustry.
April 6	Sheffield.. ..	Sheffield Society of Engineer and Metallurgists.

All but one of the meetings were addressed by the Chairman and one or more of the other members of the Committee, and the discussions which invariably followed were productive of valuable suggestions or information regarding local conditions which demand special consideration. It may be also mentioned that the Chairman lectured at the Royal Institution of Great Britain on Thursdays, January 20, 27, and February 3 last, on "The Utilisation of the Energy of Coal."

In March last the Committee was asked by the newly formed Central Coal and Coke Supplies Committee of the Board of Trade to make suggestions as to economies in fuel consumption which could be made at the present time, and, as the result of further correspondence upon the matter, it was arranged that Sir Richard Redmayne should act as the representative of the Board of Trade Committee on this Committee.

During the first year of its existence the attention of the Committee has been fully occupied with questions of organisation and a preliminary survey of the ground which must be explored later on. Already several important lines of investigation needing the co-operation of manufacturers have been instituted and are well in hand. But the returns are in most cases not yet sufficiently complete to justify publication in the Report, and, in view of the importance of the interests and issues involved, the Committee feels that it would be premature to issue any detailed report on particular aspects of the fuel question until its inquiries have reached a more advanced stage than at present.

The Committee recommends that it be re-appointed to continue its investigations, as outlined and foreshadowed in this Report, and, in view of the considerable expense involved in carrying out such work, it feels justified in asking for a grant of £100.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 2, 1916.

Dr. Alexander Scott, M.A., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society through death of:—Frederic William Caton, Charles George Edgar Parmer, and William Gilbert Saunders (killed in action); John Angell, Percy Carter Bell, Matthewman Dalton Cowap, Edward Davies, Louis Charles Deverell, William Esson, Clifford Girdlestone Gill, Ernest Alfred Lewis, Edmund George McBretney, Nicholas Henry Martin, Sir William Ramsay, Kaikhushroo Bamanji Sorabji, William Hugh Spottiswoode, Edwin Whitfield Wheelwright.

In speaking of the irreparable loss the Society and the whole world had sustained in the death of Sir William Ramsay, the President stated that he had served on the Council for twenty-three years in all, being Foreign Secretary from 1902 to 1907, and President from 1907 to 1909. He also referred to the honours that had been conferred upon Sir William Ramsay from all countries, and to his strong personality and social charms.

Certificates were read for the first time in favour of Messrs. Frederick William Atack, M.Sc., 88, Claude Road, Chorltonville, Manchester; Syed Mahomed Azain, B.A., 19, Stanhope Gardens, South Kensington, S.W.; Douglas Heriot Baird, Halidon, Esher, Surrey; Gerrard W. Baker, 3, Haling Park Road, South Croydon; Charles Samuel Bedford, Rocella, West Park, Headingley, Leeds; William Alfred Benton, 91, Allen Road, Wolverhampton; Stephen Bernard Bowyer, 36, Christchurch Road, Streatham Hill, S.W.; Ralph Eustace Brett, 43, High Street, Homerton, N.E.; Leslie Norman Brown, 109, Barclay Road, Warley Woods, Birmingham; Arthur Sidney Carlos, B.Sc., 42, Foxley Road, North Brixton, S.W.; Herbert Charles Cocks, 89, Cairo Road, Walthamstow, N.E.; Norman Cooke, Daylesford, 23, Woodville Grove, South Reddish, Stockport; Henry Edward Cox, B.Sc., 451, Glossop Road, Sheffield; Alfred William John Denney, 99, Haldane Road, East Ham, E.; Arthur Fairbourne, M.Sc., Research Department, Royal Arsenal, Woolwich, S.E.; George James Francis, 27, Rectory Road, Barnes, S.W.; Daniel Gardner, Sabalkanski, 26/49 kv. 5, Petrograd, Russia; Stanley Frederick Garrard, B.Sc., 367, Lower Addiscombe Road, Croydon; Sir Robert Abbott Hadfield, F.R.S., 22, Carlton House Terrace, S.W.; Archibald John Hall, B.Sc., 50, Fitzroy Road, Primrose Hill, N.W.; John Allen Harker, D.Sc., F.R.S., Alston, Queen's Road, Teddington; William Charles Harris, Tayside, Mill Park, Hornchurch, Romford; Charles Harrison, 137, Avondale Square, Old Kent Road, S.E.; Cedris Stanton Hicks, M.Sc., Ravensbourne, Dunedin, Otago, New Zealand; Herbert Hobson, 44, Yarburgh Street, Whalley Range, Manchester; Edward John Holness, Belle Vue, Park Crescent, Milton Road, Portsmouth; Percy Claude Cameron Isherwood, Ph.D., Moss Cottage, Bushey Heath, Watford; John Jaques, 66, Grove Road, Wanstead, N.E.; John Lea, 9, Corinthian Avenue, Stoneycroft, Liverpool; George Lodge, care of Messrs. Levinstein, Ltd., Blackley, Manchester; Francis Eric Milsom, B.Sc., 35, Elvendon Road, Palmer's Green, N.; Cosmo Murray, Canna, Cowper Street, Waverley, N.S.W.; William George Palmer, B.A., B.Sc., St. John's College, Cambridge; Richard Garnet Penney, 11, High Street, Hull; John Pomphrey, 39, Leeds Old Road, Bradford; Arthur Walter Richardson, 28, Avenue Road, Southall; Arthur Villiers St. Armande, Mount Saterland, Nitshill, Glasgow; Herbert Savage, 48, Portsdown Road, Maida Vale, W.; Charles Adalbert Schunck, Ewelme, near Wallingford; Neville Steele, Overdale, Langley, Macclesfield; Arthur George Surfleet, 221, Anlaby Road, Hull; Edwin Taberner, B.Sc., H.M. Factory, Gretna, Carlisle; Crozier Fullerton Tofts, care of Loco. Superintendent, G.I.P. Railway Co., Parel, Bombay, India; Frederick Alfred Unwin, 6, Balfour Road, Ilford; Adolph William Henry Upton, Brooklyn, Tavistock Road, South Woodford, N.E.; Ernest Edward Wallen, 15, Woodstock Drive, Bolton.

The following papers were read:—

"Theory of Vegetable Tanning." By H. R. Procter and J. A. Wilson.

"Notes on some Oxalates." By Alexander Scott.

"The Dual Theory of Acid Catalysis. A Comparison of the Activities of certain Strong Acids." By H. M. Dawson and T. W. Crann.

Ordinary Meeting, November 16, 1916.

Dr. Alexander Scott, M.A., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of Messrs. John Ferguson, David Howard, and John Peden.

Certificates were read for the first time in favour of Messrs. His Highness Raj Rana Sir Bhawani Singh Badahur, Jhalrapatan, India; Ernest Graham Bainbridge, M.Sc., 6, Schubert Road, Putney, S.W.; William Reading Bufton, Barton Lodge, Broomy Hill, Hereford; Norman Mederson Comber, B.Sc., No. 2 Training Reserve Battn., Rugeley Camp, Staffs.; Harold James Cross, 41, Athenlay Road, Nunhead, S.E.; Sir William Coats Cross, Bart., Marchbank Wood, Beattock, Dumfriesshire; John Dines, 23, Shenley Road, Dartford; John Sydney Keel, B.Sc., Malvern College, Worcestershire; Samuel Sugden, 27, Stokenchurch Street, Fulham, S.W.

The following Certificates have been authorised by the Council for presentation to ballot under By-law I. (3):—Sher Singh Sawny, M.Sc., Rawalpindi Raja Bazar, India; Leo Federovitsh Iljin, Imperial Military Medical Academy, Petrograd; Alexej Evgrafovitsch Favorsky, Royal University, Petrograd.

The following papers were read:—

"A Simple Method of Estimating Arsenic in Organic Derivatives." By A. J. Ewins.

"The Hydrolysis of Iron Ammonium Alum." By W. N. Rae.

"The Resolution of Asymmetric Quinquivalent Nitrogen Compounds. Part I. The salts of *d*- and *l*-Phenylbenzylmethylallylammonium Hydroxide with *d*- and *l*-α-Bromocamphor-π sulphonic Acid." By J. Reilly.

FARADAY SOCIETY.

Ordinary Meeting, November 8, 1916.

Sir Robert Hadfield, F.R.S., President, in the Chair.

(Concluded from p. 282).

Mr. J. Allen Howe made a statement on the "*Recent Work of the Geological Survey on Refractory Materials.*"

The statement indicated what the Survey has done since the war in preparation for the forthcoming Report on British Refractory Materials. The country has been blocked out into field-areas, and from each samples of raw materials have been secured and classified, the geological character of their locality and the nature of the deposits having been exactly noted. In each main centre both producers and users of refractory materials have been consulted. The main groups of material may be classified as the silica group, the fire-clay group, refractory sands, and dolomite, and the report will probably be issued in corresponding sections. Well over 1500 samples have so far been received, and the collection of the raw material—the first stage of the work—is almost completed. The next stage, putting into shape the field-notes and the chemical, petrological, mineralogical, and textural examination of the specimens, is already well advanced. Arrangements are being made to test the refractoriness and determine other physical characteristics of the materials, and the data so obtained will be included in the Report.

Dr. A. Strahan, Director of the Geological Survey, supplemented Mr. Howe's statement. After a reference to the practical value of the 6-in. Survey maps, he emphasised that the Report will tell manufacturers exactly the extent and nature of the reserves of refractory minerals in this country, and specimens for examination will be available in the museums. A selection from the samples collected was exhibited at the meeting.

Mr. T. Crook, of the Imperial Institute, in commenting upon the specimens exhibited by Dr. Wyndham Dunstan, Director of the Institute, stated that the Empire was well provided with resources in the less common refractories, such as graphite, in India and Canada; chromite, which is abundant in Rhodesia and India: magnesite in Victoria, South Africa, and British Columbia; bauxite in India and British Guiana, and zircon in Natal.

Mr. Cosmo Johns (Sheffield) dealt with the "*Use of Silica as a Refractory Material in Steel Manufacture.*"

After briefly referring to the use of refractory sands and the advantage of small amounts of impurity, the status of the silica or Dinas brick was discussed. He pointed out that owing to the fact that the raw material of the industry was never pure, the brick itself was a mineral aggregate of extreme complexity, and owing to the absence of exact knowledge as to its thermal history, it could not be treated from the simple standpoint of the binary system lime-silica. Its constitution at high temperatures could not be predicted from a petrological study of the brick before or after use in our present state of knowledge. The important changes it undergoes during long service under furnace conditions, with the accompanying absorption of magnetic oxide of iron, were mentioned, and it was suggested that though the magnetite was possibly only an indicator signifying the nearer approach to equilibrium of the original components at the high temperatures the brick had been subjected to for a long period, the possibility that the magnetite was not a passive agent was not excluded. It was suggested that the lines along which investigations might be made with the prospect of early and useful results would be the study of the effect of texture by varying the grain-size and correlating texture with such physical properties as refractoriness and ability to withstand variations of temperature. When the most suitable texture had been decided upon the investigation of the time-temperature curve during burning of the brick could be undertaken.

Mr. Albert Cliff (Stamford) spoke "*On the Manufacture of Refractory Materials,*" putting forward in a general way the makers' point of view.

Various suggestions were made as to the directions in which improvements in manufacture were possible. One was in the reworking up of old material: this would be one of the best means of eliminating expansion and contraction. In the basic and neutral groups of refractories there was an inviting prospect for the application of manufacturing skill. Some of the present temporary difficulties in the supply of materials he himself was overcoming by fastening working surfaces of chromite, magnesite, or other materials not liable to corrosion on to ordinary fire or silica bricks. Some samples of these faced bricks were exhibited. As a manufacturer he advocated the closest possible union between the chemist and the craft in the carrying out of organised investigations—mere laboratory tests were insufficient—into the commercial value of the minerals, chromite, magnesite, graphite, and others, reported that evening as abundant in the colonies. Above all, improved education was necessary in those who were to carry on the business of making refractories; the men of science must come down to them and talk to them freely of principles and facts, and so accelerate a rise of specialised intelligence among clayworkers.

Mr. E. P. Page (Sheffield), who spoke on "*The Classification of Refractory Materials and some Notes on Method and Points for Investigation,*" briefly introduced his paper as follows:—

This paper is confined in the main to the materials used in the heavy industries. To cover the whole field of refractory materials and their application in large branches of industry would be beyond the range of accomplishment in any single paper. The collection and tabulation of facts is a laborious task, since much of the information is only to be obtained by the association of those who are engaged in industrial practice. Further, the science of refractory materials is in its infancy, and much of that which is considered to be the fact requires verification. An easy method of classifying refractory materials has been to divide them into three sections, namely, acid, basic, and neutral, according to their chemical composition and their behaviour towards each other and the acid or basic compounds brought into contact with them under such conditions as are favourable for reaction to take place. The classification is somewhat arbitrary, because a clay such as china clay must be expected from its chemical composition to be a neutral material, which experience shows is not the case, and it is customary to include all refractory clays in the acid class. The essential property of any material claimed to be refractory is stability at the temperatures to which it is exposed, with sufficient reserve of stability to resist chemical and mechanical influences externally applied. The first quality is a classification of pure refractoriness, and the second is one of refractoriness plus skill in application. However, since purely basic or purely acid conditions seldom exist, the successful issue is generally the result of compromise, a certain degree of refractoriness *per se* being sacrificed in favour of an increase of refractoriness against other things. Materials belonging to the acid class are always used where it is a case of refractoriness towards heat, because they are widely distributed and comparatively low in first cost and lend themselves rightly to adaptation to all purposes. Suitable basic and neutral materials, on the other hand, are not so widely distributed, and possess in important instances inherent properties which render them difficult of application.

Mr. W. J. Jones, of the Ministry of Munitions, said the discussion had brought out clearly the necessity for closer co-ordination between science and practice, between the laboratory on the one hand and the brick-maker and the steel-maker on the other. It was the enormous increase of production necessitated by the war that had brought home to the steel industry the importance of their refractory materials. He urged as a further reason for co-ordination the different results that so often were obtained with the very same material in different works.

Mr. A. A. McDougall Duckham, of the Ministry of Munitions, also emphasised how much the output of munitions depended on refractories. It was clear that we had at home and in the Empire ample material to enable us to hold our own,

Dr. W. Rosenhain, F.R.S., of the National Physical Laboratory, spoke of the necessity for paying attention to the highest class of refractories now that metallurgists, especially in the electric furnace, were utilising very high temperatures. Metallurgists should know all about materials like carborundum, alundum, silicon, and similar products now being produced at Niagara Falls. There was great promise in zirconia, especially the highly purified material. An analysis of crude zirconia (about 75 per cent pure) was given. This material fell far short of pure ZrO_2 in refractoriness, but still bricks made of it would resist temperatures up to 1600° C. To get the best results it was essential to shrink the material at a much higher temperature than that it would have to stand eventually, particularly because it was so bad a conductor of heat. The crude zirconia was greatly improved by removing the chief flux, namely, the iron oxide, with hydrochloric acid. Zirconia bricks as now purified for optical purposes do not frit until well over 2000° C. Dr. Rosenhain went on to discuss the cracking of refractories. This was caused by physical forces involving nothing but determinable constants, and the *coefficients of thermal endurance* could be worked out, as had been done for glass.

Prof. T. Turner (Birmingham) reminded the meeting that the subject was also of interest to the glass, pottery, and porcelain industries, and he referred to the work on glass being done at Sheffield University. Speaking of the relation between porosity and the packing of the grains of which the material is built up, he pointed out that round grains did not necessarily mean an open and sharp a close packing. Small round particles in the interstices of larger round ones, as one might have in sand, gave the closest grain. Porosity had been measured by drawing air through at a known rate.

Dr. R. S. Hutton (Sheffield) pleaded for more work at the very high temperatures of the electric furnace. For example, the properties of completely shrunk magnesia were quite different from those of ordinary calcined, and the shrinking could be economically effected electrically.

Dr. W. H. Hatfield (Sheffield) remarked on the work to be done on the resistance of refractories to slag erosion. He gave examples of the great disparity in behaviour of different grades of silica bricks. Before more progress was possible much more accurate instruments for registering high temperatures were necessary; at present, calibration between 1000° and 2000° C. was difficult and uncertain.

Prof. F. G. Donnan, F.R.S., spoke of the necessity for a standard quantitative specification for silica bricks.

Dr. P. G. H. Boswell, of the Geological Department, Imperial College of Science and Technology, read a paper on "*Refractory Sands.*"

Many of the sands used for refractory purposes are not true sands in the geological sense; they frequently contain a proportion of refractory clay, &c. There is no doubt that we can replace from home resources a large proportion of the refractory sands hitherto imported from abroad, but the extent to which this can be done will not be completely known until further investigation of the properties of suitable materials and satisfactory substitutes has been carried out. The admirable work of H.M. Geological Survey in collecting, recording, and, in part, subjecting to analysis supplies of refractory materials worked in this country needs to be supplemented by much research work, for in certain directions the properties of desirable sands, for example, are not fully known, and geologists do not know what to look for. Pure academic work in the shape of the application of modern petrographic methods to the investigation of sands is urgently required, but the final tests of the suitability for particular purposes must always be on a commercial scale in the works. On the academic side, we need far more results of experiments and observations carried out on certain definite lines and under standard conditions, with continuity secured by the retention of one worker or set of workers in each direction. The time has passed for the scattered and haphazard methods and results of which we have had so large a number. The pure scientific work will indicate the likely materials to be tried in industrial practice and will eliminate the improbable. The closest British analogues to the very suitable foreign materials will then be found.

The refractory sands used in industry may be divided into three chief classes:—(*a*) The high silica sands (with 98·99 or more per cent of SiO_2), (*b*) the high silica and alumina sands bearing variable proportions up to 20 per cent alumina, as kaolin, &c., and little else but silica, (*c*) sands for greensand-moulding, carrying a strong and highly refractory natural clay bond. All class (*a*) sands hitherto imported may be replaced from the abundant and excellent British supplies. (The economic factors, freight, &c., will have to be considered). We have also valuable deposits of class (*b*), but so far as those sands of class (*c*) which are used for high temperature steel-moulding are concerned, it must be admitted that the best of foreign sands hitherto used here have not been equalled by known British resources. The reason for this is twofold: in the first place the peculiar properties of the Belgian red or yellow sands, to take a concrete case, have never been thoroughly investigated with the view of finding substitutes; in the second, we do not yet know all our British sand and related deposits at all thoroughly. At least two geological horizons in this country should be thoroughly searched in this connection: they are the Pliocene and the Lower Cretaceous. The Tertiary and Cretaceous deposits of the south-west of England are particularly deserving of attention.

In brief, research on British and foreign refractory sands is desirable in the following directions (among others):—

(i.) Mechanical analyses, to gain more accurate ideas of grading, carried out scientifically.

(ii.) Chemical analyses of each grade, not bulk analyses.

(iii.) Mineral analyses, to realise the importance of constituent minerals, especially those prone to decomposition which yield the "bonds" of these sands.

(iv.) The water-holding capacity at 10° intervals at temperatures below 110° and at suitable but greater intervals above.

(v.) The conductivity.

(vi.) The refractoriness of each grade.

(vii.) Pore space and permeability.

It is to be hoped that before long a detailed account of British resources of refractory sands, with analyses and notes on their peculiar properties, may be in the hands of manufacturers and others. Such a report by the speaker on British resources of sands suitable for glass-making, with notes on certain highly siliceous materials suitable for refractory purposes, was just being published at the request of the Ministry of Munitions. These glass-sands fall under classes (*a*) and (*b*) above, but the resources suitable for refractory purposes are far larger than those for glass-making.

Finally, co-ordination of the work of the four classes of interested people (users of refractories, the makers of refractories, the collectors and analysts of raw materials, and the research workers) is urgently required to prevent serious overlapping and to ensure a minimum loss of effort and a maximum of benefit to the country, which as far as possible should be self-supporting in the matter of raw materials for key-industries.

The General Discussion was resumed by —

Mr. E. Kilburn Scott, who confirmed from his own experience with flame-arc furnaces what Dr. Hutton had said about the possibility of completely shrinking magnesite.

Dr. W. C. Hancock spoke of the application of certain organic dyes to etch refractory materials much as metals were etched. This method, coupled with Prof. Fearnsides', would be a powerful weapon for elucidating internal structure. He was working on coke-oven firebricks in this direction in conjunction with Prof. Bone at the Imperial College of Science and Technology.

Here the President called on Mr. Ezer Griffiths, M.Sc., of the National Physical Laboratory, to read his paper on "*The Thermal Conductivity of Materials Employed in Furnace Construction.*"

The paper dealt with the methods employed for investigating the thermal conductivity of bricks and tiles of commercial sizes.

One of the practical difficulties was the attainment of a uniform temperature over the hot face of the sample, since the surfaces were always irregular. It was found possible to obtain good thermal contact, as well as a very uniform distribution of temperature over the surface, by the use of a shallow bath of molten metal electrically heated.

In high temperature experiments the heating was effected by making the test sample a part of the walls of a large muffle.

The heat transmitted was measured by a flow calorimeter fitted with a guard ring.

A compact form of thermo-element was described: the two wires (Pt – Pt 10 per cent Ir) being separately insulated by silica capillaries and both enclosed in a silica sheath of about 5 mm. diameter. The sheath was closed at the end in the form of a bulb containing the junction. The thermo-element was employed for exploring the distribution of temperature in the metal bath, and for this purpose it was bent into an L shape.

Values of the thermal conductivity and its variation with temperature were given for two typical materials employed for thermal insulation—the one composed principally of diatomaceous earth baked at a high temperature to form a rigid brick of friable texture, the other manufactured by blowing steam through molten blast-furnace slag, which converts it into a product bearing a resemblance to cotton-wool. This material was tested in the form of a mat, the faces being covered with wire meshing.

Dr. J. A. Harker, F.R.S., commented on the value and accuracy of Mr. Griffiths' work on a subject presenting serious experimental difficulties.

He added some information on the properties of zirconia, which, if fine enough, would stand being plunged into water at a white-heat temperature.

Written communications to the Discussion were received from—

Mr. W. Donald (Glasgow), who sent in some specimens of raw and calcined Greek magnesite and magnesite cement and bricks, wrote that they were having to make substitutes for Austrian magnesite bricks, and they were therefore adding some 8 per cent Fe_2O_3 to the Greek magnesite, which was too pure, to approximate its composition to the Austrian. Mr. Donald also exhibited some Indian and Rhodesian chrome ore and cements and bricks made therefrom. He went on to suggest that the use of dolomite in conjunction with magnesite for basic steel furnaces needed serious consideration. He believed that when, as often, the dolomite boils with the metal, active ferrates of lime may be formed, and the result is destructive to the magnesite foundation of the furnace. He had recently suggested to the Iron and Steel Institute the desirability of drawing up standard specifications for bricks used in the iron and steel industries. Finally, he touched on the question of linings for electric furnaces, and he incidentally mentioned the possibilities of Serbia, with its minerals and plentiful water-power, as an electro-metallurgical centre.

Mr. A. B. Searle (Sheffield) expressed his agreement with the view that chemical analysis was secondary in importance to some of the physical characteristics of firebricks, and he had himself chiefly relied on physical and microscopical methods of examination. Referring to the desire for co-ordination that had been expressed, he reminded the meeting that they had a trade journal which devoted special attention to the scientific and technological aspects of refractories. Backwardness was largely due to the fact that most of the firms concerned were too small to undertake research work. Furthermore, research, to be useful, must be carried out by specialists who had practical knowledge of the industry. The manufacturers should combine together and retain such men, leaving the Universities to concentrate on questions of academic interest, for which they were specially fitted.

Mr. T. Allen (Dudley) said the great difficulty in making improvements in manufacturing processes in this industry was to prove the value of any change, because this might take years to realise. Laboratory tests were often inconclusive. Nevertheless, the gas retorts of to-day were meeting the severe demands put upon them. An important point was the economy of not running retorts after their efficiency has dropped, say in one thousand to two thousand days. He did not think German or American gas installations showed better results than the best of our own. He paid a tribute to the work of the Refractory Materials Committee.

Mr. F. Deansfield (Oldham) wrote of the desirability of inducing manufacturers to adopt more uniform methods. He also drew attention to the enormous loss of refractory clays lying under coal seams, due to the winning of the coal only, so that it afterwards becomes too dangerous and costly to win the clay. These msterials should be carefully reserved, if necessary by legislation. He hoped the Society would consider this problem.

Mr. Alleyne Reynolds wrote that he knew of an Austrian works having clamped arches of silica bricks 8 ft. in width that had been in use for over twenty years, whereas we were satisfied to produce silica bricks with 20 per cent expansion. The same firm paid more attention to properly heating their ladles and shaping their nozzles than any British firm of his acquaintance. There should be more co-operation between the steel-makers and the makers of refractories. The keeping of so-called "trade secrets" was to be deprecated; the most successful manufacturers were rhose who showed, like their President, a large-minded scientific spirit. Mr. Reynolds disagseed with the President as to worn clay nozzles accounting for slag inclusion in steel ingots, which he thought resulted from reactions in the dissolved FeO and FeS. He was suspicious of magnesite nozzles, from which minute particles would probably be carried into the mould. He added some interesting information on the proper method of casting steel from the ladle and on the effect of iron oxides in firebricks. Fe_2O_3 and Fe_3O_4 seem to increase the refractoriness of bricks exposed to oxidising atmospheres; any iron oxide is detrimental in reducing atmospheres. The bricks forming the regenerators of open-hearth furnaces take up much more iron in the gas than in the air chambers, and their regenerative efficiency is increased. The subject needs proper investigation, as does also the volatilisation of refractories, particularly magnesite, at low temperatures, such as 1300° C., perhaps due to catalytic action. A properly designed electric furnace was, he thought, the only remedy.

Mr. Charles R Darling, in view of the relatively high conductivity of fire-bricks as shown by Mr. Griffiths, drew attention to the suggestion of Hutton and Beard, made before the Society in 1905, that furnaces should be lagged with a highly insulating substance. Experiments by Fitzgerald and by him had confirmed the great saving anticipated. It was strange that metallurgists had not adopted the idea.

A very useful refractory was alundum, of which Messrs. Baird and Tatlock exhibited specimens. It melted at

2050° C., and had no action on platinum at high temperatures, so was suitable for platinum-wound electric furnaces. A non-porous variety was useful for sheathing pyrometers and is less corroded by molten metals than silica. The question of the electrical conductivity of refractories had been little studied; in a research he was engaged upon he needed one that was non-conducting at 1600° C. and which was not easily attacked by metallic oxides.

A considerable number of specimens of minerals and refractory materials and products were exhibited to the meeting by the authors of the papers and others.

MISCELLANEOUS.

Change of Address.—Messrs. Henry Faija and Co., of Portland Cement Testing Works and Chemical Laboratories, 6, Earl Street, Westminster, S.W., announce that notwithstanding notification of their removal from 41, Old Queen Street, Westminster, to the above address was posted in December last, letters and samples are frequently received at the old offices. They desire, therefore, to again direct attention to the address of the premises they now occupy.

Messrs. Abdulla and Co., Ltd., Almanac for 1917.—When twelve months ago we called attention to a Patriotic Almanac then issued by the above firm, in aid of the British Red Cross Society, we did not expect that the same effort would be again necessary. Unhappily, the war is still with us, and the funds of the Red Cross are in greater need than ever. We must congratulate Messrs. Abdulla upon this happy method of advertising their cigarettes, providing a useful and interesting almanac, and adding materially to the funds of such an important institution. The almanac contains twelve good reproductions of works of the best artists, and is as far above the usual run of trade productions as their very excellent wares are above the mass of cheap material that pass under the name of cigarettes. 20,000 copies are again to be devoted to the funds of the British Red Cross Society. Copies can be obtained from any tobacconist, or post free in the United Kingdom from Messrs. Abdulla and Co., 186, New Bond Street, at 1s. 4d. per copy; one shilling will be paid into the "funds" for every copy sold.

British Pharmacopœia Standards for Exported Drugs and Chemicals.—The Chemical Trade Section of the London Chamber of Commerce desires to give publicity to the fact that the attention of the British exporters of drugs and chemicals has been drawn by a Government authority in Australia to the desirability that all drugs and chemicals exported from the United Kingdom shall be in all respects up to the British Pharmacopœia standards. It is believed that German exporters, before the war, complied strictly with this condition, and it is therefore suggested that if business is to be maintained after the war the correct standard of quality must be strictly adhered to by British firms, especially in view of the probability that enemy countries will, at all costs, make strenuous efforts to renew those business relations which they have temporarily lost.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer, in the Chair. His Excellency M. Paul Painleve and Vito Voltorra were elected Honorary Members of the Royal Institution; and Neville Bayly, William D. Mitchell Cotts, Mrs. Maude Dickinson, Arthur L. Gibson, and Arthur Keith were elected Members.

Royal Institution.—The Ninety-first Illustrated Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. Arthur Keith, M.D., F.R.C.S., LL.D., F.R.S., his title being "The Human Machine which All Must Work." The subjects are as follows:—Living Engines, Dec. 28; Living Levers, Dec. 30; Living Pumps, Jan. 2; Living Bellows, Jan. 4; Living Workshops, Jan. 6; Living Central Exchanges and Wires, Jan. 9. The Lecture Hour is 3 o'clock. The following are the lecture arrangements before Easter:—Prof. C. S. Sherrington, six lectures on "The Old Brain and the New Brain and their Meaning, and Pain and its Nervous Basis"; Prof. W. E. Dalby, two lectures on "The Structure of Metals"; Prof. J. W. Gregory, three lectures on "Geological War Problems"; Prof. Sir Walter Raleigh, two lectures on "The Strength and Weakness of Romantic Poetry"; Prof. F G. Donnan, three lectures on "The Mechanism of Chemical Change"; two lectures by Prof. Edward S. Prior; Prof. A. Dendy, two lectures on "Sponges—A Study in Evolutionary Biology"; Prof. J. A. Fleming, two lectures on "Modern Improvements in Telegraphy and Telephony"—(1) Telegraphy, (2) Telephony; Arthur R. Hinks, two lectures on "The Lakes and Mountains of Central Africa"; Dr. H. Walford Davies, three lectures on "Line and Colour in Music"—(1) Piano, (2) Strings, (3) Voices; Daniel Jones, two lectures on "The Science of Speech"—(1) The Pronunciation of Languages in General, (2) The Pronunciation of English at the time of Shakespeare; Dr. C. W. Saleeby, two lectures on "Imperial Eugenics"; Stephen Graham, two lectures on "Russian Idealism"—(1) The Russian Madonna, (2) The Ideas of the Russian Philosopher Vladimir Solovyof. The Friday Evening Meetings will commence on January 19, when Prof. Sir James Dewar will deliver a Discourse on "Soap Bubbles of Long Duration." Succeeding Discourses will probably be given by Prof. Gilbert Murray, Charles C. Carpenter, Daniel Jones, Rev. H. Hensley Henson, H. Wickham Steed, Charles F. Cross, Sir Almroth Wright, Sir J. Stirling Maxwell, Edward Clodd, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 8th.—Faraday Society, 8.

Tuesday, 19th.—Institution of Petroleum Technologists, 8. "Notes on the Subject of Geological Mapping," by S. Lister James.

Thursday, 21st.—Chemical Society, 8. "Studies on the Walden Inversion—Part V., The Kinetics and Dissociation Constant of α-Bromo-β-phenylpropionic Acid." by G. Senter and G. H. Martin. "The Alcohols of the Hydroaromatic and Terpene Series—Part III., The Isopulegols corresponding with *l*-Menthol and *d*-Neomenthol," by R. H. Pickard, W. Lewcock and H. de Pennington. "Lead Sub-iodide, with Details of the Preparation of Lead Suboxide" and "Note on the Solubility of Lead Iodide," by H. G. Denham. "Chromium Phosphate," by A. F. Joseph and W. N. Rae.

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THE CHEMICAL NEWS

Vol. CXIV., No. 2978.

THE SOLUBILITY OF MINERAL PHOSPHATES IN CITRIC ACID.

Part II.

By G. S. ROBERTSON, M.Sc.

Varying opinions have been held regarding the value of mineral phosphates as a phosphatic manure since their introduction some seventy years ago by Professor Daubeny and Captain Widdrington. The advent of superphosphate and basic slag has done much to keep the value of mineral phosphates in the background.

Ground mineral phosphate costs from 9d. to 11d. per unit of phosphate, whereas basic slag costs 2s. per unit. If the phosphates in rock phosphates are as efficient as those in basic slag, and there is every reason to suppose they are, their economical importance is obvious.

The advent of basic slag was followed by the introduction by Wagner of what is now known as the "citric acid test." Wagner showed that from 70 to 95 per cent of the phosphate in basic slag was soluble in 2 per cent citric acid in half-an-hour, and he brought forward the results of field experiments which demonstrated that the field returns from basic slag were proportional to the solubility of the phosphate as judged by the citric acid test.

The citric acid test has been semi-officially adopted in this country, and many British manufacturers of basic slag are following the trade practice of the German firms by selling slag according to the citric solubility of the phosphate.

Mineral phosphates are only slightly soluble in citric acid, and as many agriculturists have accepted the theory that phosphates insoluble in citric acid are of little value to the plant, any attempt to espouse the cause of rock phosphates is heavily handicapped. This is all the more remarkable as not a tittle of reliable evidence exists in support of this theory.

The manurial value of mineral phosphates, however, can only be definitely established by the experience of the farmer. In this respect experiments carried out at Cockle Park in 1911—1913 are interesting (see "Cockle Park Guide," 1915, p. 39). In these two experiments Belgian and Tunisian phosphates have given results strictly comparable with the highest citric soluble basic slag. In this connection it is interesting to note that, in the U.S.A., mineral or rock phosphates are used almost to the exclusion of basic slag.

In a previous paper (*Journ. Soc. Chem. Ind.*, 1914, xxxiii., No. 1) the author was able to show that Belgian and Tunisian phosphates were completely soluble in 2 per cent citric acid, provided sufficient time was spent on the extraction. As so much stress has been laid upon the "citric acid test," this work has been considerably extended. The citric solubility of several other classes of rock phosphates has been determined, and also the effect upon the solubility of the phosphate of fineness of grinding and calcining.

Table I. shows the total analysis of the various phosphates used.

Whenever the hardness of the phosphates permitted, it was ground and divided into several portions by means of the 1 mm. sieve and sieves with 30, 60, 90, and 100 holes to the linear inch. Each of the five portions was submitted to five consecutive half-hour extractions with 500 cc. of 2 per cent citric acid. The extract was filtered by means of a filter-pump, a Hirch filter-funnel, and a 7 cm. diameter filter-paper. The filtration usually occupied less than five minutes.

Makatea Island Phosphate.

This phosphate is of a particularly hard nature, and it is therefore surprising that in the portion passing "100" sieve over 90 per cent of the phosphoric acid is soluble in the 2 per cent citric acid extracts. The figures given in Table II. clearly show, assuming citric solubility to be a test, that fine grinding, which aids even distribution in the soil, would have much to do with the value of the phosphate as a manure.

Five grms. of the portion passing the "100" sieve was calcined for four hours. (A Fletcher muffle furnace was used for calcining all the phosphates mentioned in this paper). Five consecutive extracts with 500 cc. of 2 per cent citric acid were made with the calcined phosphate. The calcining process decreased by 22 per cent the total solubility of the phosphate—or, judging by the citric acid test, by 7 per cent.

Florida Pebble Phosphate.

There appeared to be no calcium carbonate in this sample, and the effect of fineness of grinding was therefore determined.

The results recorded in Table III. closely agreed with those obtained with Makatea Island phosphate. It is interesting to note that the difference in solubility (judged by five extractions) between any two consecutive portions is approximately 10 per cent. The slightly higher percentage of phosphoric acid dissolving in the second extracts of portions "refuses 60" and "refuses 100" is partly due to a slight disintegration of the phosphate in the shaker, and partly to the presence of a small amount of calcium carbonate in these portions.

Five grms. of the phosphate was calcined as in previous cases. To remove any free lime the calcined portion was shaken for four hours with 500 cc. of a 10 per cent solution of cane-sugar, containing 10 cc. of absolute alcohol, before the citric extracts were made.

Of the mineral phosphates examined, this is the only one which shows an increased solubility as the result of calcining. The noticeable rise in the phosphoric acid dissolving in the second extract is curious. This matter has been further investigated, and it would appear that the phosphate dissolving in the first citric extract is in combination with silica, whilst that dissolving in the second, third, fourth, and fifth citric extracts is precisely the same as the phosphate contained in Makatea Island phosphate — whose solubility is greater than Florida pebble phosphate.

The results with Algerian, Gafsa, Tunisian, and Belgian phosphates are given in Table IV.

It is worthy of note that a comparatively small percentage of calcium carbonate greatly decreases the solubility of the phosphate as judged by the citric acid test, whilst upwards of 30 per cent of calcium carbonate makes the phosphate practically insoluble, judging by the citric acid test.

For purposes of comparison samples of bone-meal and apatite were submitted to consecutive extractions with 2 per cent citric acid (Table V.). Owing to difficulty experienced in filtering the extracts the bone-meal was first gently ignited to destroy most of the organic matter).

Table V.—*Passes "100" Sieve.*

	Bone-meal.		Apatite.	
	P_2O_5, per cent.	Per cent of total.	P_2O_5, per cent.	Per cent of total.
First extract .	26·69	73·11	1·28	3·24
Second ,, .	9·29	25·46	1·70	4·33
Third ,, .	0·51	1·43	1·47	3·72
Fourth ,, .	—	—	1·47	3·72
Fifth ,, .	—	—	1·30	3·29
Extract totals	36·49	100·00	7·22	18·30
Actual totals .	36·49	100·00	39·49	100·00

TABLE I.

	Mineral phosphates.							
	Makatea Island.	Florida pebble.	Algerian.	Gafsa.	Tunisian.	Belgian.	Apatite.	Bone meal.
Calcium oxide	52·38	47·10	46·13	43·30	48·40	50·55	55·45 (*b*)	50·28
Phosphoric acid	38·24	31·50	27·27	25·35	26·13	19·80	39·49	36·49
Carbon dioxide..	1·69	3·04	6·70	5·50	9·03	17·22	2 23	4·76
Moisture	1·46	1·00	0 72	3·26	0 98	—	—	—
Combined moisture and organic matter	3·39	2·41	3·28	4·39	3 21	3 60	—	6·82 (*c*)
Ferric and aluminium oxides	1·01	1·60	2·59	4·98	4·25	1·09	—	—
Magnesium oxide	1·35	1·90	2·02	1·72	0·90	1·14	—	0·66
Sand	0·28	7·03	8·12	7·56	4·65	4·28	0 38	0·26
Undetermined	0·20	4·42	3·17	3·94	2·45	2·32 (*a*)	2·45	0·73
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100 00

(*a*) Including sulphate, 1·02 per cent. (*b*) Partly combined with fluorine and chlorine. (*c*) Organic matter.

TABLE II.

Extraction.	Refuses 1 mm. sieve.			Refuses "30" sieve.			Refuses "60" sieve.		
	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.
First	3·93	5·40	10·10	4·98	7·00	12·67	6·40	9 00	16·31
Second	3·66	5·10	9·31	4·85	6·70	12·36	6·06	8·85	15·40
Third	3·47	4·80	8·91	4·56	6·40	11·11	5·44	7·52	13·87
Fourth	3·28	4·55	8·43	3·84	5·33	9·71	4·77	6·72	12·13
Fifth	2·91	4·10	7·48	3·70	5·20	9·43	4·30	6·00	10·96
Extract totals . ..	17·25	23·95	42·23	21·93	30 63	55·28	26·97	37·80	68·67
Actual totals	38·90	53·38	100·00	39·24	53·75	100·00	29·23	53·90	100·00

	Refuses "90" sieve.			Passes "100" sieve,			Passes "100" sieve. (Calcined).		
First	7·47	10·65	19·02	9·25	13·01	24·16	6·58	9·50	17·25
Second	7·07	9·90	18 02	8·26	11·46	21·58	6·32	8·58	16·55
Third	5·95	8·40	15·17	7·54	10·50	19·70	5·55	7·51	14·52
Fourth	5·46	7·50	13·92	6·03	8·55	15·75	4·63	6 29	12·10
Fifth	4·82	6 70	12·29	4·22	5·75	10·02	3·79	5·16	9·94
Extract totals . ..	30·77	43·15	78·42	35·30	49·27	91·21	26·87	37·04	70·36
Actual totals	39·09	53·57	100·00	38·24	52·38	100·00	38·24	52·38	100·00

TABLE III.

Florida Pebble Phosphate.

Extraction.	Refuses "30" sieve.			Refuses "60" sieve.			Refuses "100" sieve.			Passes "100" sieve.		
	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.
First . ..	4·00	5 98	12 02	4·36	6·62	13·37	5·10	7 78	16·02	6 18	9·23	19·61
Second ..	3·81	5·74	11·45	4·48	6·66	13·74	5·27	7·78	16·56	5·83	8·76	18·51
Third ..	3·63	5·38	10·91	4·25	6·32	13·03	4 92	7·40	15·46	5·46	8·24	17·33
Fourth ..	3·23	4 90	9 71	3·86	5·81	11·84	4·52	6 60	14·20	5·14	7·72	16·31
Fifth ..	3·00	4 63	9·02	3·69	5·40	11·32	3 89	5·72	10·65	4·31	6·36	13 68
Extract totals ..	17·67	26·63	53·11	20·64	30·81	63·30	23·70	35·28	72·89	26·92	40·31	85·44
Actual totals ..	33·27	49·13	100·00	32·61	47·90	100·00	31·83	48·30	100·00	31·50	47·10	100·00

Calcined Florida Pebble, passes "100" Sieve.

	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.
1st sugar extract	—	0·10	—
First citric extract	6·01	9·56	19·08
Second „	6·77	10·00	21·49
Third „	6·63	9·07	21·05
Fourth „	5·49	7·58	17·43
Fifth „	3·88	5·44	12·33
Extract totals	28·78	41·75	91·38
Actual totals..	31·50	47·10	100·00

TABLE IV.—*Portions passing "100" Sieve.*

	Algerian.			Gafsa.			Tunisian.			Belgian.		
	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.
First extract	6·65	12·92	24·40	10·15	17·94	40·00	4·83	14·37	18·48	1·95	17·30	9·75
Second ,, ...	6 98	11·04	25·53	8·18	13·14	31·99	7·81	11·84	29·39	5·65	11 73	28·25
Third ,, ...	5·35	8·60	19·60	5·60	8·80	21·54	5·83	8·84	21·97	5 78	10·14	28 90
Fourth ,, ...	4·00	6·30	14 63	1·93	2·97	7 61	4·40	6·62	16 84	4·95	7·90	24·60
Fifth ,, ...	2·47	3·94	9·08	—	—	—	2·93	4·30	11·06	1·99	3 13	9·65
Totals for five extracts .	25·45	42·80	93·24	25·86	42·85	101·14	25·80	45·97	97·74	20·32	50·20	100·15
Actual totals..	27·27	46·13	100 00	25·35	43·30	100·00	26·13	48·40	100·00	19 80	50 55	100·00

The results obtained after calcining the various phosphates are given in Table VI.

TABLE VI.—*Calcined Phosphates* (*passes* 100 *Sieve*).

(Free lime removed by sugar solution).

	Algerian.		Gafsa.		Tunisian.	
	P_2O_5, per cent,	Per cent of total.	P_2O_5, per cent.	Per cent of total.	P_2O_5, per cent.	Per cent of total.
Citric extraet—						
First . ..	3·33	12·21	5·20	20·50	4·46	17·06
Second ..	4·36	15·99	6·55	25·87	4·58	17·55
Third . ..	3·78	13·86	5·77	22·80	3·54	13·55
Fourth ..	3·10	11·37	4·49	17·75	2·56	9·81
Fifth . ..	2·29	8·40	2·29	9·07	2·07	7·93
Extract totals	16 86	61·83	24·30	95·99	17·21	65·90
Actual totals	27 27	100 00	25·35	100·00	26·13	100 00

Calcined Algerian, Gafsa, and Tunisian phosphates show a very marked decrease in citric solubility due to calcining. The author has been able to show that the decrease in solubility in each case is due to the production of a small quantity of a citric soluble silico-phosphate (with a higher lime content than the original phosphate) which goes into solution in the first citric extract, whilst the remaining extracts contain phosphates with a lower lime content than the original phosphate, and which are therefore less soluble in citric acid. But there is no reason to suppose that because the calcined phosphates are less soluble in citric acid they are of less value to the plant than the corresponding uncalcined phosphates.

Calcined Belgian Phosphate.

Two 5-grm. portions of this phosphate were calcined, the first portion for about four hours in a furnace to which it was afterwards discovered the gas supply was partially choked. The second portion was calcined in a hotter furnace, it not being thought at the time that any difference in the composition of the two portions would be produced thereby. The object of the experiment was to discover to what extent the free lime produced by calcining interfered with the citric solubility of the phosphate. The second calcined portion was therefore extracted with sugar solutions before being submitted to the citric acid extractions.

A glance at the totals soluble in five citric extracts (Table VII.) shows that the higher temperature to which Portion 2 was raised has had an effect on that portion which was not produced on Portion 1. It is obvious in the case of this Belgian phosphate that the higher the calcining temperature the more insoluble does the phosphate become. Portion 1, in spite of the fact that the first citric extract contains practically no phosphate, has more phosphate soluble in the five citric extracts than Portion 2, which has had all the free lime removed before the citric acid extracts were made.

Although the figures do not accurately reflect the effect of free lime in decreasing the solubility of the calcined phosphate as judged by the ordinary citric acid test, they are of sufficient accuracy to show that the presence of about 18 per cent of free lime in a calcined Belgian phosphate makes it practically insoluble in citric acid.

TABLE VII.—*Calcined Belgian Phosphate.*

	First portion. (Passes ' 100 '' sieve).			Second portion. (Passes '' 100 '' sieve)		
	P_2O_5, per cent.	CaO, per cent.	Per cent P_2O_5 of total.	P_2O_5, per cent.	CaO. per cent.	Per cent P_2O_5 of total
Sugar extract—						
First . ..	—	—	—	—	17·32	—
Second ..	—	—	—	—	0·61	—
2 per cent citric extract—						
First . ..	0·56	20·04	2·80	3·57	7·80	17 85
Second ..	6·15	9·68	30·75	4·73	6 98	23·65
Third ..	5·61	8·42	28·05	4 28	6·20	21·40
Fourth ..	4·75	7·02	23·75	3·16	4·53	15·30
Fifth . ..	2·52	3·80	12·60	2·14	3·08	10·70
Extract totals	19·59	48·96	97·95	17·88	46·52	88·90
Actual totals	19·80	50·55	100·00	19 80	50 55	100·00

Conclusions.

The results undoubtedly show that mineral phosphates are completely soluble in 2 per cent citric acid if a sufficient number of extracts are made. In the majority of the rock phosphates examined five extracts removed 90 to 100 per cent of the phosphoric acid present.

Even a small amount of free lime or calcium carbonate decreases substantially the solubility of mineral phosphates as judged by the citric acid test. When a large amount of calcium carbonate or free lime is present, the citric acid test, as commonly practised, is a test for lime and not for phosphates. It is important in this respect to distinguish between free lime and calcium carbonate and lime actually entering into the composition of the phosphate. The higher the percentage of lime actually entering into the phosphate compound, the higher the citric solubility of the phosphate.

Fineness of grinding affects the total citric solubility of the mineral phosphates (judged by five extracts) to the extent of approximately 10 per cent decrease for each of the gradients—passes "100," refuses "100," refuses "60," and refuses "30" sieve.

With one exception, calcining produces a marked decrease in the citric solubility of mineral phosphates. The longer the calcining continues the more insoluble does the phosphate become.

The results, judged as a whole, confirm the conclusion arrived at as the result of a previous investigation (*Journ. Soc. Chem. Ind.*, 1914, xxxiii., 9), namely, the worthlessness of the citric acid test as a means of judging the relative value to the plant of phosphatic manures. Rock phosphates are quite as soluble in a ½ per cent hydrochloric acid solution as basic slag, and there is just as much reason in favour of using a weak solution of a mineral acid for a solvent as there is for using a 2 per cent citric acid solution.

It would be absurd to consider basic slag as of no agricultural value because it is insoluble in water, and it is equally absurd to condemn mineral phosphates because they are not so soluble in citric acid as basic slag.

There can be little doubt that, as a source of phosphoric acid for the plant, rock or mineral phosphates are just as valuable as basic slag.—*Journal of the Society of Chemical Industry*, xxxv., No. 4.

FUEL ECONOMY.[*]

(Concluded from p. 290).

Appendices.

The Work of the Sub-Committees.

The following memoranda concerning the work of each of the five Sub-Committees will sufficiently indicate the various matters which are at present chiefly under consideration, and the arrangements which have been made for their future investigation. (The Chairman and Secretary of the General Committee are *ex officio* members of each Sub-Committee).

A.

Chemical and Statistical Sub-Committee.—Dr. J. T. Dunn (Chairman), Prof. P. P. Bedson, Dr. W. Galloway, Prof. Thos. Gray, Mr. T. Y. Greener, Prof. L. T. O'Shea, Sir Richard Redmayne, Dr. A. Strahan, and Dr. R. V. Wheeler.

The Sub-Committee is preparing a memorandum and a bibliography upon the question of the chemistry of coal, and is of the opinion that the time has now arrived for a re-investigation of the subject in order to clear up a number of outstanding points connected with the chemical constituents of coal, their mutual relations in the raw material, and their influence upon the character of the various products obtainable by its distillation or oxidation. Accordingly, some of its members have undertaken experimental work, partly on new lines and partly by way of check repetition, with the object of providing a basis for a more complete attack upon the subject in the near future. A group of research assistants is already working on the problem under Prof. Bone's direction in the Department of Chemical Technology of the Imperial College of Science and Technology, London.

As an important part of the work the Sub-Committee hopes later on to organise systematic investigations upon the chemical character of the principal British coal seams. Such an undertaking would, however, involve considerable labour and expense, and the prospect of achieving any useful result will depend entirely on the amount of funds which may be forthcoming in support. The Sub-Committee is of the opinion that the resources both of existing laboratories which have been established within recent years in this country for the special investigation of fuel problems, and of other laboratories where the technique of the subject has been developed, might be utilised more than they are at present in this connection, and that the time is ripe for the organisation of a scheme of systematic co-operative research, aided by national funds, in which all such laboratories may participate.

The Sub Committee is also compiling statistical information relative to the different purposes for which coal is used, and has entered into communication with the Board of Trade upon the question, but the collection and analysis of such statistics has been greatly impeded by the war.

Another important matter into which the Sub-Committee proposes to inquire is the amount of wastage due to coal which, for one reason or another, is at present left behind in the pits. Part of such wastage, for example, that due to the occurrence of faults in the coalfields, is unavoidable, but when all such allowance has been made, there undoubtedly remains a large wastage in working which might be and ought to be avoided. A memorandum is being prepared on the reduction of such wastage by the adoption of hydraulic stowing, a practice which, although in vogue on the Continent, has not yet been established in Great Britain.

B.

Carbonisation Sub-Committee.—Mr. T. Y. Greener (Chairman), Prof. P. P. Bedson, Sir G. T. Beilby, Mr. E. Bury, Dr. Charles Carpenter, Dr. J. T. Dunn, Prof. Thos. Gray, Mr. D. H. Helps, Mr. C. H. Merz, Prof. L. T. O'Shea, Dr. J. E. Stead, Mr. G. Blake Walker, and Dr. R. V. Wheeler.

The total amount of coal carbonised in this Kingdom for the manufacture of metallurgical coke or for towns' gas in the year 1913 was probably about thirty-five to forty million tons, or approximately one-fifth of the total home consumption of coal for all purposes.

According to a recent Parliamentary Return relating to all Authorised Gas Undertakings in the United Kingdom, the total quantity of coal carbonised for towns' gas by 831 such undertakings in the year 1913 amounted to 16 971,724 tons, from which 195,826 million cubic feet of coal gas were produced, or, say, on the average, about 11.500 cubic feet per ton of coal carbonised. There are a number of gasworks not included in this Parliamentary Return, and it is computed that they carbonise about one and a quarter million tons of coal per annum. Thus the total coal carbonised in gasworks throughout the Kingdom in the year 1913 would be about 18,200,000 tons.

The amount of ammonium sulphate produced by gasworks in that time in the United Kingdom was officially given as 182,180 tons, which on the above basis would represent an average yield of about 22·4 pounds per ton of coal carbonised.

No such complete returns are available in relation to the manufacture of metallurgical coke, but the amount of coal carbonised for this purpose in 1913 probably did not fall much short of twenty million tons. Of this coal, the larger proportion was carbonised in by-product ovens, producing, besides coke, tar, benzol, &c., some 133,816 tons of ammonium sulphate. Assuming an average yield of 22·5 pounds of ammonium sulphate per ton of coal, it would appear that approximately 13·3 million tons were carbonised in by-product ovens, and probably about half that amount in bee-hive ovens.

With regard to the coking industry, the Sub-Committee has already undertaken steps to secure a complete return of the number of by-product recovery ovens installed and working throughout the country, the character of each installation (whether waste heat or regenerative), its coking capacity, the description of the recovery plant connected with it (whether direct or indirect), the number of benzol recovery plants in operation, the quantities and yields of the by-products obtainable, and the purposes for which waste heat and surplus gas are being employed. When completed, this return will enable the Committee to arrive at an approximate estimate of the margins of possible economies in the shape of improved utilisation of the coal carbonised which can now be effected in the coking industry and the directions in which further progress is likely to be made.

A memorandum is also in course of preparation describing the more important developments of the by-product coking industry, from its inception until the present day

With regard to gasworks practice, inquiries have been instituted regarding the present practice in connection with the manufacture of towns' gas, and for this purpose the Institution of Gas Engineers is officially represented on the Sub-Committee. It is also intended later on to consider the question of low-temperature carbonisation from the point of view of its possible economic results, but up to the present time so little authentic information is available that the Committee would welcome the offer of proper facilities to enable them to investigate the matter.

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[*] First Report of the Committee (Prof. W. A. Bone, Chairman; Mr. E. D. Simon, Secretary). Read before the British Association (Section B), Newcastle Meeting, 1916.

C.

Metallurgical, Ceramic, and Refractory Materials Sub-Committee.—Dr. J. E. Stead (Chairman), Mr. Robert Armitage, M.P., Prof. J. O. Arnold, Sir Hugh Bell, Bart., Mr. E. Bury, Sir Robert Hadfield, Mr. Greville Jones, Dr. J. W. Mellor, Mr. Robert Mond, Mr. Bernard Moore, Mr. Benjamin Talbot, Mr. B. W. Winder, and Mr. H. James Yates.

The amount of coal consumed in metallurgical, ceramic, refractory materials, and cognate industries probably amounts to approximately 20 per cent of the total home consumption. Of this, probably about three-fourths must be debited to the iron and steel industries.

The Sub Committee has taken steps to ascertain from some of the larger manufacturers data which will assist it in determining the actual amount of fuel which is being used on the average in the manufacture of the various brands of pig-iron, spiegeleisen, ferro-manganese, &c., throughout the Kingdom. A memorandum is in preparation concerning the heat balance of a blast-furnace of modern construction for the manufacture of Cleveland No. 3 and other pig-irons, and a description will be given of the best methods now available for the utilisation of the surplus gases from such a furnace. Inquiries are also being made as to the results of the application of dry air to blast-furnaces.

In like manner a series of questions relative to fuel consumptions in steelworks has been prepared for circulation among the larger steel plants in the Kingdom, with a view to ascertaining both the present average consumption and the directions in which further economies may be looked for in the near future. In this connection the Sub-Committee will endeavour to draw up a statement as to the best lay-out and arrangement of a combined by-product coking, iron-smelting, and steel-making plant from the point of view of utilising as completely as possible surplus gases and waste heat, and thus realising the maximum fuel economy in the heavy-steel industry.

Similar inquiries will be instituted in regard to present-day practice and results in relation to (1) iron foundries, (2) manufacture of wrought iron, and (3) specialised steel industries.

Two members of the Sub-Committee specially connected with the ceramic industry have undertaken to prepare a memorandum showing the average present practice and the possible margins of fuel economy in relation to that industry, and information is invited by the Sub-Committee relative to glass-works and brick-works.

The Sub-Committee desires to state that all information communicated to it by individual manufacturers will be regarded as confidential, and will be used merely as a basis for arriving at an approximate estimate of the present average fuel consumption per unit of output in the particular industry to which the information relates.

(Note.—It is suggested that all such information should be sent in the first instance to Prof. Bone, Chairman of the General Commitee, at the Imperial College of Science and Technology, London, who will classify and summarise it under either alphabetical letters or numerals in such a way that the names of the manufacturers or firms concerned will not be divulged to any of the members of the Committee).

D.

Power and Steam Raising Sub Committee.—Mr. C. H. Merz (Chairman), Lord Allerton, Mr. J. A. F. Aspinall, Dr. Dugald Clerk, Mr. S. Z. de Ferranti, Sir Robert Hadfield, Dr. H. S. Hele-Shaw, Mr. W. W. Lackie, Mr. Michael Longridge, Mr. Robert Mond, Hon. Sir Charles Parsons, Prof. Ripper, Mr. R. P. Sloan, Mr. C. E. Stromeyer, Prof. Threlfall, Mr. G. Blake Walker, and Mr. B. W. Woodhouse.

The special duty of this Sub-Committee is to investigate the economies in fuel which would result from the use of improved methods, and it has been decided to deal with the subject under the following heads:—

1. To consider (*a*) the amount of fuel consumed, and (*b*) the corresponding power developed in the United Kingdom, under the following heads:—Factories, Mines, Railways, Ships, and Steam Raising for other purposes than power.
2. To consider the present position of central electrical power plants and gas undertakings as regards power supply.
3. To discuss the relative merits of the present methods for producing power by steam, gas, oil, and petrol engines respectively.
4. To investigate the possible saving of fuel which might be effected (*a*) by improved plant, (*b*) by greater centralisation of power production, (*c*) by co-ordination with metallurgical and other manufacturing processes, (*d*) by some measure of public control, (*e*) by better supervision, and (*f*) by the use of inferior grades of fuel which are at present wasted.

While, on account of the magnitude of the subject and the amount of investigation involved, it is not possible at present to submit any report, it may be mentioned that information has been sought as to the amount of fuel consumed and the corresponding power developed in such official publications as the Report of the Royal Commission on Coal Supplies in 1905, the Census of Production for the year 1907, and the Returns published annually by the Home Office for Mines and Quarries, and various Shipping and Customs Reports. But although, from such sources fairly accurate figures can be obtained for the amount of coal used annually for industrial purposes and shipping, the corresponding figures of power produced are not obtainable from any published returns so far as can be ascertained.

The average figure of five pounds of coal per horse-power hour which was given in the Report of the Royal Commission on Coal Supplies in 1905 was, we believe, deduced from a number of typical industrial concerns where information could be obtained, and it is probable that this estimate did not exaggerate the actual coal consumption per horse-power hour at that time.

In view of the impossibility of obtaining accurate returns of fuel consumption per horse-power hour from the whole of the power users in this country, it has been decided to investigate the matter by asking for detailed returns from typical factories in various trades and in different districts throughout the country, selected by members of the Sub-Committee who have special knowledge of particular trades.

Special memoranda are in course of preparation on questions of organisation of power production for industrial and transport purposes, the use of large turbine and gas engines, and other important aspects of the power question.

E.

Domestic Fuel Sub-Committee.—Mr. E. D. Simon (Chairman), Mr. A. H. Barker, Prof. H. B. Dixon, Prof. W. W. Haldane Gee, Prof. W. P. Wynne, and Mr. H. James Yates.

The amount of coal actually consumed for domestic purposes in the United Kingdom probably does not fall far short of thirty-six million tons per annum—nearly one-fifth of the total consumption for all purposes in the Kingdom. To this would have to be added the "coal equivalent" of the gas and electricity consumed for domestic purposes, if a correct estimate of the total domestic coal consumption is to be made. The Royal

Commission of 1905 estimated that 50 per cent of the coal consumed for domestic purposes might be saved by the installation of better appliances, so that there is clearly a vast field for economy.

The whole question of domestic uses of fuel bristles with difficulties and complications. In the first place, it is necessary to discriminate between fuel or energy consumed in the kitchen for cooking and other similar purposes and that applied for the heating of ordinary living-rooms.

In the vast majority of the houses inhabited by the artisan population the kitchen fire or stove is the only place in the house where fuel is burnt; also in better-class houses it is only in the kitchen that fuel is burnt daily throughout the whole year. Hence it would appear that the kitchen is responsible for the greater part of our annual domestic fuel bill, and therefore the question of the relative efficiencies of kitchen ranges, gas and electric cookers, and hot-water supply apparatus assumes considerable importance.

Again, the selection or recommendation of particular means or apparatus for domestic heating cannot always be based simply upon the question of thermal efficiency, because it also involves considerations of a physiological and even of a psychological character. Thus, for example, systems of central heating which have been recommended, on grounds chiefly of thermal efficiency, and which are so universally used in America and on the Continent, are not usually acceptable to the average Englishman, who undoubtedly prefers to be warmed by the radiation from a bright fire.

This being so, the Sub-Committee feels that it will be wise to recognise at the outset that there is probably no single solution of the domestic heating problem which is likely to be universally adopted within any measurable period of time, and that therefore it should preferably concentrate its efforts upon questions of more immediate practical importance.

It will be generally agreed that any reform in domestic fuel consumption should aim at achieving one or more of the following objects, namely:—

(1) Actual reduction in cost of domestic heating, either in the form of direct saving of fuel or labour, or both;
(2) Mitigation or abolition of the domestic smoke nuisance; and
(3) Better hygienic conditions in living-apartments generally.

The Sub-Committee can perhaps best discharge its duties by considering how far the various systems now available for domestic heating fulfil such requirements, and how they may severally be installed and operated to the best advantage.

In order to do this the Sub-Committee has arranged for experiments to be carried out with the object of determining how to produce in a given room suitably warm and healthy conditions at a minimum cost, and with a minimum production of smoke, and how such conditions may be defined for any particular room. Also, experimental work is being carried out upon the relative efficiencies of coal fires, gas fires, electric heaters, and the like.

Inasmuch, however, as in this country the use of the open coal fire will probably continue for some time to come, and as there are undoubtedly great economies to be immediately realised by the wider adoption of improved fire-grates, the Sub-Committee will pay special attention to the question of improvements in the construction and Installation of such grates, to which the attention of architects, builders, and the public generally ought to be drawn.

Arising out of the present extensive use of solid fuel in domestic fires, the Sub-Committee will also consider the important question of the prospects of substituting for raw coal some form of carbonised fuel (semi-coke or coke). There can be no doubt but that if such a substitution could be effected, without either increasing the domestic coal bill or involving some other disadvantage, not only would there be a great addition to the amount of valuable by-products annually obtained from coal consumed in the Kingdom, but also the smoke nuisance in our large centres of population would be materially reduced.

Work on these lines is being carried out in the Department of Heating and Ventilating Engineering at the University College, London, at the Municipal School of Technology, Manchester, and at the Department of Chemical Technology at the Imperial College of Science and Technology, London.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.*

The Electrolytic Determination of Cadmium in Cadmium Bromide.

By GREGORY PAUL BAXTER, MERRITT ROY GROSE, and MINER LOUIS HARTMANN.

Recently the atomic weight of cadmium has been redetermined by Baxter and Hartmann (*Journ., Am. Chem. Soc.*, 1915, xxxvii., 113; *Zeit. Anorg. Chem.*, xcii., 53) in the T. Jefferson Coolidge Memorial Laboratory of Harvard College by the electrolytic analysis of cadmium chloride. By using a glass electrolytic cell of special design it was found possible to deposit the metal in a mercury cathode directly from the solution of the salt. The results of this work fully substantiate the value for the atomic weight of cadmium previously established in the Harvard laboratory by Baxter, Hines, and Frevert (*Journ. Am. Chem. Soc.*, 1905, xxvii., 222; 1906, xxviii., 770; xliv., 158; xlix., 415) through comparison of the chloride and bromide of cadmium with silver. Both methods yielded the result 112·417 (Ag = 107·880). The electrolytic analysis of cadmium chloride was instigated by investigations by Perdue and Hulett (*Journ. Phys. Chem.*, 1911, xv., 1579), Laird and Hulett (*Trans. Am. Electrochem. Soc.*, 1913, xxii., 385), and Quinn and Hulett (*Journ. Phys. Chem.*, 1913, xvii., 780; *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1997), who have recently obtained a considerably lower value, 112·3, by the electrolytic analysis of cadmium sulphate and cadmium chloride, and cadmium bromide, and by the comparison of simultaneous deposits of silver and cadmium. In order to obtain further evidence on the subject, the analysis of cadmium bromide by an electrolytic method similar to that employed by Baxter and Hartmann has been carried out. The results of this work confirm very closely all the earlier work in the Harvard Laboratory. Just as the sum of the percentage of chlorine in cadmium chloride found by Baxter, Hines, and Frevert, and the percentage of cadmium found by Baxter and Hartmann is 100·000, so the sum of the percentage of bromine in cadmium bromide found by Baxter, Hines, and Frevert, 58·708, and the percentage of cadmium is determined in the present research, 41·290, is 99·998. It is difficult to imagine more convincing evidence of the accuracy of the two methods of analysis.

Purification of Reagents.

Water, nitric acid, sulphuric acid, alcohol, and mercury were purified by Baxter and Hartmann (*loc. cit.*). In a few experiments mercury, which had been not only three times distilled in vacuum, but also once at low pressure in a current of air, was used. No difference in the behaviour of the two samples could be detected. Bromine was freed from impurities by the processes used by Baxter and Grover (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1029), and from the pure bromine hydrobromic acid gas and its solution were prepared by synthesis with pure electrolytic hydrogen in the same way and with the identical apparatus employed by Baxter and Grover.

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* *Journal of the American Chemical Society*, xxxviii., No. 4.

Purification of Cadmium Bromide.

Since in the earlier work Baxter and Hartmann found that crystallisation of cadmium bromide is a very rapid and convenient method of freeing cadmium from metallic impurities, this method of purification was used in preparing the salt for the present purpose. Non-metallic impurities, such as silica and organic matter, were eliminated both by crystallisation and by fusion of the salt in an atmosphere of nitrogen charged with hydrobromic acid gas.

Sample A was prepared from crude cadmium, containing lead and traces of copper and thallium, by cleansing the metal superficially and dissolving it by treatment with the purest bromine under dilute hydrobromic acid solution in a Jena flask. The excess of bromine was removed by boiling, and after filtration through platinum sponge, the solution was evaporated in a platinum dish to crystallisation. The salt was five times re-crystallised. Since even then the salt, upon fusion, yielded a small amount of black insoluble matter which has been shown elsewhere (Baxter and Hartmann, *Journ. Am. Chem. Soc.*, 1915, xxxvii. 121; Baxter and Grover, *Ibid.*, 1915, xxxvii., 1040) to consist chiefly of carbon and silica, the whole was fused in platinum boats contained in a quartz tube in an atmosphere charged with hydrobromic acid gas, in the fashion described later. The insoluble matter was removed by solution and filtration through platinum sponge, and the salt was twice more crystallised in platinum vessels. The product, when fused, yielded little, if any, of the black residue.

In all the crystallisations the salt was centrifugally drained in platinum Gooch crucibles (Baxter, *Journ. Am. Chem. Soc.*, 1908, xxx., 286), and the evaporation of the solutions was carried out upon electric stoves, in order to avoid contamination from the products of combustion of illuminating gas. Sample A was used in Analyses 1 and 3.

To prepare Sample B the metal was first transported electrically from an anode of commercial cadmium through an electrolyte of very concentrated cadmium bromide solution to a platinum wire cathode, where it was deposited in the form of a crystalline mass. In this way carbon and other non-metallic impurities was very largely eliminated. Since, however, it is impossible to wash clean an electrolytic deposit of the nature of that obtained in this process, the precaution was taken of using for the electrolyte cadmium bromide which was free from chloride. As a matter of fact, the electrolyte was prepared from the mother-liquors of Sample A. The mass of crystals was washed by decantation as thoroughly as possible by prolonged treatment with pure water, and then was converted into bromide by covering it with very dilute hydrobromic acid solution in a quartz flask, and adding freshly distilled bromine. The resulting solution of bromide was then boiled for several hours in contact with a small amount of the purified metal in order to precipitate as far as possible the more highly electro-positive metals. Next, the solution was filtered through a platinum sponge crucible, held in a platinum funnel, into a platinum dish, and was evaporated to crystallisation. After the product had been once re-crystallised from pure water in platinum it was fused in platinum boats in a quartz tube in an atmosphere of nitrogen highly charged with hydrobromic acid gas. Since the fused salt contained a small amount of the black insoluble material it was now dissolved in water, and the solution was again filtered through platinum sponge. Then the solution was evaporated to crystallisation, and the product was three times more re-crystallised from the purest water, all in platinum vessels with the utmost care to avoid the introduction of dust. The product was perfectly white, and gave after fusion in an atmosphere containing hydrobromic acid only a trace of the black residue.

In order to find out whether foreign metals had been successfully eliminated, a portion of the salt was dissolved in a mimimum amount of water, and metal deposited from it upon a platinum cathode as completely as possible, with the use of a platinum anode also. The crystals were washed very thoroughly and dried in a vacuum desiccator. Then the metal was fused in a hard glass tube in a current of hydrogen gas, and while still fused drawn up into capillary tubes of hard glass. In order to prevent the metal from sticking to the capillary tube the inside of the capillary was lightly coated with soot by drawing a luminous flame into the tube. If this is done the glass is very easily cracked from the metal wire thus formed. The spark spectrum was then produced from these electrodes, and photographed in a Féry quartz spectrograph, in which the range $\lambda\,2100$—$\lambda\,6000$ is covered. The spectrum showed no lines other than those usually associated with cadmium, and was identical in every way with the spectrum of the purest material prepared by Baxter and Hartmann.

Sample C of cadmium bromide was prepared in essentially the same manner as Sample B. Sample C was probably purer than any of the others, for upon fusion it yielded least of the black residue, some of the specimens being entirely free from any visible matter of this kind. Sample B was used in Analyses 2 and 4, Sample C in Analyses 5 and 11.

By good fortune a small amount of cadmium bromide remaining from the earlier research by Baxter, Hines, and Frevert had been preserved in a dry state in a sealed glass tube. This material is designated in the earlier research, Samples II. and III. On fusion in hydrobromic acid this material yielded a small amount of the black residue of carbon and silica, but no more, judging from the appearance and recent experience in this laboratory, than 0·001—0·002 per cent. This is designated Sample D in the table of results. Some of the sulphate from which this bromide had been prepared, also remained. Metal prepared from this sulphate gave a spectrum free from the lines of foreign metals.

Preparation of the Cadmium Bromide for Analysis.

To prepare the cadmium bromide for weighing it was fused in a dry atmosphere charged with pure hydrobromic acid gas. The salt was contained in a quartz boat, and this in turn was placed in a transparent quartz tube, which formed part of a "Bottling apparatus" such as is usually employed in this laboratory for transferring a boat to a weighing bottle without exposure to moisture (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59; *Zeit. Anorg. Chem.*, xiii., 85). The hydrobromic acid gas was prepared by synthesis from pure bromine and hydrogen in the same apparatus and in exactly the same way as in a research upon lead bromide by Baxter and Grover (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1035). In the earlier experiments the fusion atmosphere was prepared by passing pure nitrogen through fuming hydrobromic acid solution, and then, in order to remove moisture, over fused calcium bromide. In many of the final series of experiments the fusion atmosphere consisted of hydrogen which had been charged with hydrobromic acid in the same way. No difference in the appearance or the composition of salt fused in the two atmospheres could be detected.

Previous to fusion the cadmium bromide was freed from a portion of its crystal water in a vacuum desiccator containing fused potassium hydroxide. Then, after the greater part of the residual water had been expelled at a low temperature by heating the salt in the hydrobromic acid atmosphere, the temperature was gradually raised by means of an electrically heated sleeve until the salt was fused. As soon as the salt had solidified, the fusion atmosphere was displaced with pure nitrogen, and this finally with pure dry air, and the boat and contents were transferred to the weighing bottle in which they were to be weighed, without exposure to the outside air. (The air and nitrogen were purified and dried as described by Baxter and Grover, *loc. cit.*).

The quartz boats with their weighing bottles were found to remain unaltered in weight by the treatment during fusion. This confirms earlier experience in this laboratory and elsewhere.

(To be continued).

SCIENCE AND INDUSTRY, WITH SPECIAL REFERENCE TO THE WORK OF THE NATIONAL PHYSICAL LABORATORY.*

By R. T. GLAZEBROOK, C.B., M.A., D.Sc., F.R.S.,
Director of the National Physical Laboratory.

THE subject is a wide one, even when limited by the special reference. It has been much discussed lately, and the Report of the Privy Council Committee for Scientific and Industrial Research published in September last has brought to the fore many of the problems that need solution, if we wish to place at the disposal of the nation all that Science can contribute to the good of Industry.

I hope to show you to-night that the National Physical Laboratory has assisted in the progress of the past ten or fifteen years, and that by its development we should gain a powerful instrument to aid us in the future.

The Advisory Committee of the Privy Council was appointed to consider, among other objects, proposals "for establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades.

The earlier clauses of its first Report deal with previous Government action in the present century; let me commence by quoting them :—

> "Certain events which preceded the establishment of the Council are worthy of record because they are now seen to have a general significance which was not realised at the time. As early as 1900 the Government had taken an important step in the encouragement of organised scientific support for our trades and industries. The National Physical Laboratory was then established, with the assistance of a grant from the Treasury, under the control of the Royal Society, and opened in 1902 by His Majesty the King, then Prince of Wales. 'I believe,' he said on that occasion, 'that in the National Physical Laboratory we have almost the first instance of the State taking part in scientific research. The object of the scheme is, I understand, to bring scientific knowledge to bear practically upon our everyday industrial and commercial life, to break down the barrier between theory and practice, to effect a union between science and commerce. This afternoon's ceremony is not merely a meeting of the representatives of an ancient and world-renowned scientific Society for the purpose of taking over a new theatre of investigation and research. Is it not more than this? Does it not show in a very practical way that the nation is beginning to recognise that if her commerial supremacy is to be maintained greater facilities must be given for furthering the application of science to commerce and manufacture?' It is nearly half a generation since these wise and far-sighted words were spoken; to-day they certainly convey more to the whole nation than they did when the Government made its first modest capital grant of £13,000 for the buildings and equipment of the Laboratory and an annual allowance for maintenance of £4000 for five years (*a*). His Majesty's pregnant summary of the national need might, indeed, have been addressed to the Advisory Council, for it expresses admirably the conviction with which we have begun our labours. The Laboratory has done, and is doing, most valuable work for our industries and for the Government, and it might have done much more had it been endowed with anything like the annual subvention of nearly £100,000 which the American Bureau of Standards receives for development and maintenance from the United States Government (*b*). But we think experience has shown that no single institution, however great or distinguished, can expect to do more than a part of all that our vast industries require."
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> (*a*) The grant was gradually Increased to £7000, at which figure is has remained since 1908-9. In addition, a grant varying from year to year and amounting to £14,400 for 1916-17, is made for Aeronautical Researches.
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> (*b*) *Cf.* Report of Board of Trade Delegates to Sixth Congress of International Association for Testing Materials (1912), Cd. 7185.

It was remarked in connection with the work of the Privy Council Committee that had the Laboratory since 1902 been really placed in a position to do the work indicated by His Majesty the task of the Committee at the present day would be much lighter, and the advances already made still more considerable.

> "The object of the scheme is to bring scientific knowledge to bear practically upon our everyday industrial and commercial life."

In this process, as we shall see, and has been well pointed out by various recent writers—see Dr. Rosenhain's paper before the West of Scotland Iron and Steel Institute, "The National Physical Laboratory, Its Work and Aims"; Dr. Mees' pamphlet on "Science and Industry," issued by the Advisory Committee of the Privy Council—three distinct stages may be observed. We need :—

1. The work of the man of science in his Research Laboratory.
2. The investigations which go on in an Industrial Research Laboratory, developing new processes or introducing new products.
3. The Works Laboratory proper controlling the quality of raw materials, finished products, and processes.

Let us note then, in the first place, we must have scientific knowledge. That point I need not labour, but note also that to be successful that knowledge must be pursued for its own sake. Each of the modern practical applications of science had its foundations in purely scientific work, and to quote Prof. Gregory, in his recent book, discovery or the spirit and service of science, was not the result of deliberate intention to make something of service to humanity. It is hardly necessary to illustrate this; let me, however, give one classical example. The discovery of the laws of electromagnetic induction is due to Faraday, and is described in his first three series of "Experimental Researches," published in 1831-33. Oersted, Ampère, and Arago had investigated some of the phenomena connected with the magnetic force produced by an electric current, and to Faraday it appeared clear that conversely it should be possible to produce electricity from magnetism, as he put it. It is difficult to picture the world to-day without electric power, and yet the whole development of electrical machinery, as we know it, rests on the laws described in these brief scientific papers. Each advance of knowledge brings its benefits to mankind, and in a general way Faraday may have hoped to be a benefactor to his race by widening the sphere of knowledge, but it was the desire to know the truth which led him on and to which we owe such tremendous consequences.

We must have the student of pure research, the genius who goes on his way discovering new truths, irrespective of consequences, laying bare more and more of nature's secrets and unravelling her mysteries.

In England we have never lacked such men, our roll of great discoverers has been a glorious one. Too frequently their lives have been hard and difficult; prophets without honour they have lived; to-night it is not my task to speak of them beyond urging the importance of giving every encouragement to such men by supporting in the most generous spirit, any among you here in your University or elsewhere who are advancing the bounds of knowledge, searching for truth in some of its difficult byways. The endowment of pure science is essential; without it the attempt to apply science to industry fails.

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* Address delivered to the Birmingham and Midland Institute, on December 4, 1916.

This, however, is not my subject to-night; let us turn for a short time to the third need among those enumerated above—the Works Laboratory proper. My audience will appreciate perhaps more fully than I can the need for this.

It is necessary, if for no other reason, to maintain the standard of the output, to secure that the proper grade of material is supplied to the Works, to check the instruments in use, and to test the product in its various stages of manufacture. The days are gone when successful manufacture could be carried on entirely by rule of thumb, trusting to the skill of some trained workman for the success of each delicate operation, when the hereditary instinct passed down from father to son was sufficient to produce each year practically the same results. New processes come, which appear likely to improve production or to reduce its cost; the Works Laboratory serves to test these. New products are suggested, which may or may not have the advantages claimed for them; this can be investigated in the Works Laboratory, and all these investigations and tests must go on in the works themselves under the eyes of men familiar with the process of manufacture in its every stage. The Works Laboratory must extend, and others are more competent than I to outline the direction of extension and to guide its growth.

Now between these two—the man of science researching in his University or College, and the works chemist toiling in his shop—there is a gap. Some means are needed to make the discoveries of science available to the manufacturer to secure to him the advantages which come from the growth of knowledge to keep him in the forefront of his trade. This, if I grasp the problem aright, is the function of a Laboratory of Industrial Research, and among such laboratories the National Physical Laboratory should hold a prominent place. The National Physical Laboratory has another function to fulfil, it is a great standardising and testing institution. I will recur again to that aspect of its work; for the present let us consider what is required in a Laboratory for Industrial Research and see how far these requisites are supplied at Teddington. Quoting again from Dr. Mees' paper, already referred to, "The kind of research work," he says, "involves a laboratory very different from the usual Works Laboratory, and also investigations of a different type from those employed in a purely industrial Laboratory. It means a large, elaborately equipped and heavily staffed laboratory engaged largely on work which for many years will be unremunerative, and which for a considerable time after its foundation will obtain no results which can be applied by the manufacturer."

This work clearly needs a special House, it cannot be done in the Laboratory of a Technical Institute. The main work in such a Laboratory as that of a Technical Institute must be educational. The object of the Professor is to educate his pupils so that each may apply his knowledge to his life-work in the future. For this he will teach them to research. They will help him in his own investigations, and these may well have a bearing on the industry of the district. They may commence so solve for themselves simple problems akin to those they will meet with in their future work, but their power and opportunity to apply the new discoveries of science to the manifold problems of industry must be limited. For such work training is required, and full and elaborate equipment; the plant of a Technical School Laboratory must be designed to serve many purposes all aimed at educating the pupils to apply science, and at teaching them the methods to follow. It is not their work, while still at College, to solve the conundrums of the manufacturer. The research Laboratory is necessary if progress is to be made. Abbe realised somewhere about 1876 that British optical instruments had reached the highest possible development unless a radical change could be produced in the optical properties of glass, and the researches of Schott and himself, aided by subsidies from the Bavarian Government, lasted a number of years before the first catalogue of Jena glass was produced. Synthetic indigo was discovered by von Baeyer about the year 1880; it was not until some twenty years later that it was put commercially on the market, and in that time it is reported that no less than £1,000,000 was spent by the Badische Anilin-Soda-Fabrik before this desired end was reached.

Dr. Rosenhain in the lecture already referred to takes as an instance the case of a series of alloys which is being studied by an investigator interested mainly in theoretical metallurgy; he works with pure metals or metals as nearly pure as he can get them, and finds that one alloy of his series has some specially noteworthy properties. He may call the attention of a manufacturer to these and suggest that the alloy might have valuable industrial application. Much, however, remains to be done before this can be realised; the pure materials of the investigator are not available in quantity. To what extent is the presence of impurity detrimental, what are the impurities which must be removed, what are the steps required to do this on the requisite scale, to what extent do the difficulties involved in this render the whole method commercially impossible by adding seriously to the cost? Is there any difference between the material made in quantity and that produced by the laboratory furnace, where rapid cooling or heating may be readily employed, although impossible in the full scale work, and so on? For the industrial research laboratory the plant, &c., must be so planned that it is possible to carry out the necessary operations on a scale comparable with that required in works, and, moreover, the man who carries through the investigation must be not only acquainted with the latest scientific advances in his subject, but must know what is possible in works, and must mould his solution of the problem to harmonise with these possibilities. The undertaking is often more complex than that of the pure scientist. It is one which needs a special laboratory, a special equipment. Thus, the task of an Institution like the National Physical Laboratory differs from that of either a University or Technical Collega Laboratory or a Works Laboratory. In the first place it is not educational; every member of the staff is, it is true, learning continually, but he is not there to be taught, but to be asked questions and to find the answers. Its functions are primarily to encourage and initiate the applications of science to the problems of Industry. It is, in the words of the Order in Council already quoted, an institution for the scientific study of problems affecting particular industries and trades. The staff devote themselves solely to this work, their whole time and energy are given to it, They have no educational duties; they are free from the responsibilities of the class room and the burden of students' exercises. The senior members of the staff joined avowedly with the purpose of applying science to industry; they are prepared to make it their life-work. The juniors retain their posts for some time; thus all acquire a store of experience of the highest value, with a unique knowledge of the technical aspects of Industry which it is difficult to gain in any other way. The Laboratory has, I trust, acquired the confidence of the technical industrial world, and problems are brought before the staff with the knowledge that they will be handled in a confidential manner by men trained to deal with them. In such an institution it is possible to specialise as to both staff and equipment in a manner which can hardly be done in a laboratory attached to an educational institution. The whole staff are engaged in applying science to industry; equipment is provided for this purpose only. The needs of the students and the educational value of the apparatus have not to be considered.

Standardisation in all its branches is an important function of such a laboratory, and this involves research. The methods of measurement, the materials in which the standards can best be expressed, the accuracy of reproduction and the conditions of use all need investigation.

One other aspect of the matter remains to be considered, though very briefly. If we are to have a National Industrial Research Laboratory, who is to pay for it, who is to support it? The obvious answer is the nation, but this in some quarters at once raises a difficulty. It is claimed that the results of any successful research bring profits in the first instance to some particular class, and that class ought to pay. For example, the discovery of some new and valuable alloy would profit, in the first instance, the manufacturer of the alloy, and the persons employing it in their special trade. Before, therefore, you undertake an investigation you must secure, so it is said, the co-operation and financial support of a limited class who will presumably benefit by the success of the investigation. And no doubt as a general rule, in cases in which it can be applied, this principle is a sound one, but such cases are limited. If a manufacturer comes with a conundrum, which he desires to have answered for his own private benefit, he must pay; but if a competent committee controlling an industrial research laboratory concludes that a research is of importance and likely to lead to knowledge of benefit to the whole industry with which it is concerned, I would plead that the cost of such a research should be met out of national funds. It is very difficult to say what individual will profit most in the end. An improvement in an industrial process leading to more employment and to a cheaper method of manufacture benefits a wide circle beyond the man who introduces the process. Germany—not merely Messrs. Schott and Zeiss—has profited by the labours of Abbé and his co-workers at Jena, labours rendered possible in the first instance by State help. No doubt there are cases where the co-operation of an industry can and should be secured; sometimes, too, it will be in the public interest to protect a discovery by a patent, if only to prevent action by a private firm restricting the free use of the discovery, but, in my opinion, it is not well to hamper those who control the Laboratory by conditions aimed at securing support from industry before any special research is commenced.

The needs of the nation at the present time are too serious, the danger of delay too pressing, and the State may well devote large sums to industrial research without minute enquiry as to whether the research is going to benefit Messrs. A.B. specially and what share, therefore, of the expense Messrs. A.B. must be asked to guarantee. In America the Bureau of Standards, in Germany the Reichsanstalt and the Material-Prüfungs-Amt work thus for the national good, and this should be the task of our English Industrial Research Laboratory.

And now, having summarised briefly some of the aims and objects of the National Physical Laboratory as a Laboratory of Industrial Research, let me give some account of the place and its work during the past fifteen years, and then let me outline the task that lies before it in the future.

It was founded in 1899. My appointment as its first Director dates from January 1, 1900, but its home at Bushy House, Teddington, was not ready for it until 1902. It is controlled by the President and Council of the Royal Society, but that control is exercised through a General Board and Executive Committee containing representatives appointed by six of the great Technical Societies; at least half of the unofficial members of the Executive Committee must be selected from the representatives of these Technical Societies. The Royal Society receives from the Government the sum of £7000 annually towards the cost of the Laboratory.

In the year before the war the actual expenditure was nearly £41,000, and practically the whole of the difference between these sums had to be raised as payment for work done; towards this an amount of about £5000 was received from the Government for researches in Aeronautics. The Government also pays for tests and investigations carried out for their various Departments.

The financial responsibility for the Laboratory rests on the Royal Society. If in any year there were a serious deficit, it would fall to the Society to make it good, a risk which you will agree with me in thinking ought not to be incurred by a learned Society. As a matter of fact, the working of the Laboratory has resulted in a small balance—now amounting to some £4500—which constitutes its working capital. To run a business of £40,000 a year on a working capital of £4500 is a hazardous procedure. The fact is that the whole financial position needs overhauling. Before the war the German institutions in Berlin, which covered approximately the same ground as the Laboratory, had an income of about £70,000, while that of the Bureau of Standards of America was well over £100,000. In both these cases the Government are responsible for the whole expenditure, and take the receipts from fees.

The Laboratory owes much to private donors.

During the first fifteen years of its existence, the grants from the Treasury for capital expenditure amounted to £59,000; during the same period nearly £56,000 was received in donations and grants from various individuals and institutions, while nearly £20,000 was defrayed out of income.

Towards the annual expenditure in the same time £80,500 was received from the Treasury—the Treasury grant was originally £4000—£166,000 in fees, while £15,000 came from Grants from bodies like the Institutions of Civil and Mechanical Engineers, the Iron and Steel Institute, the Institution of Naval Architects, and private individuals. The total expenditure on Aeronautical research defrayed by Government amounted to some £33,000. These figures carry the expenditure up to March 31, 1914. Since the commencement of the war the whole Laboratory has been given up to war work, and the figures for that period would have little meaning in connection with our subject.

The Laboratory is situated at Bushy House, Teddington, an old Queen Anne House, the former home of the Ranger of Bushy Park; the last Rangers were H.R.H. the Duke of Clarence—afterwards King William IV.—and his wife Queen Adelaide, who retired to Bushy House on the King's death.

In 1902 the Laboratory consisted of an old house and a small building fitted as a Power House and Engineering Laboratory.

To-day it comprises eight large buildings, with two tall steel towers erected for experiments on wind pressure. It is organised in four main departments, each with its superintendent.

These are:—

(1) *Physics.*—Superintendent, the Director.
(2) *Engineering.*—Superintendent, Dr. T. E. Stanton, F.R.S., M.Inst. C.E.
(3) *Metallurgy.*—Superintendent, Dr. W. Rosenhain, F.R.S.
(4) *The William Froude National Tank.*—Superintendent, Mr. G. S. Baker, M.Inst. N.A.

The Physics Department is divided into six divisions, each under a Principal or Senior Assistant, and there is a large staff of Scientific Assistants, divided into Senior Assistants, Assistants, and Junior Assistants. The primary work of these is scientific research, though each is expected to take his share of the testing and examination of instruments, which forms a large part of the work of the Laboratory. Beyond these, there is a staff of Observers whose main duty is the routine test work, though opportunities are given to these to help as far as possible in the researches. The routine test work is concerned chiefly with instruments; ordinary commercial, chemical, and strength tests of materials are not undertaken by the Laboratory except for Government Departments, or as matters of special investigation.

And here let us note the importance of keeping the test work a live thing by the aid of research. Instruments are tested to see, among other objects, if they come up to standard, but the standard of to-day is too low some years hence; the tests must be so regulated as to tend to a gradual improvement in the product, and this can only be done by accompanying the tests with continuous research—research into methods of construction, into the materials most suitable for use, into the scheme of tests most helpful toward forming a correct opinion of the value of the instrument. Research must go hand in hand with testing. Without such close co-operation routine tests grow obsolete and cease to be of value; worked thus they prove an important aid to the manufacturer and a most desirable check on his production. Let me give an example of this. Ordinarily, we test a large quantity of a certain article, and the average failures are under 1 per cent—some seven or eight in a thousand. Recently, in consequence of pressure, articles were passed into service without tests, and after a time the tests were introduced; on the earliest batches examined after the change the failures were 18 per cent, they were twenty-five times as great as previously. The number of instruments tested in the year covered by the last report—to March 31, 1916—was over 75,000. This does not include gauges for the Ministry of Munitions, which in the past fifteen months have numbered nearly 250,000.

The buildings are, in the main, plain single storey brick structures with weaving shed roofs and top lights designed in each case specially for the purpose for which they are used; *e.g.*, the Metrology Building consists of an outer shell enclosing a series of interior rooms—in this way a constant temperature is maintained.

The new Administration block is an exception to this, the architect was asked to clothe it with a shell in the same style as Bushy House itself, and has done so most successfully. It was opened by Mr. Balfour in the summer of 1913.

I propose now to ask your attention to a number of slides illustrating our various activities. (Slides from photographs of the buildings and interiors and of the apparatus were here shown).

And now I have tried to show you, in brief outline, how the National Physical Laboratory endeavours to be a Laboratory of Industrial Research.

I trust I have convinced you—probably you did not need convincing—that such laboratories are necessary.

There must be more than one; in many cases an industry can be best served by a laboratory near its principal centre. Large firms, again, may each prefer to have their own trade secrets—this must be so to some extent—and trade jealousies may interfere with full co-operation, but a private laboratory on a really sufficient scale is expensive; too often it becomes little more than what I have called a Works Laboratory for testing the products of the factory, and for the smaller firms, at least, the only way to secure the full advantage of scientific advance is by co-operation—co-operation in the laboratory, co-operation, with specialisation in production, in the works themselves.

There is much for us all to do, and I ask your active support to make the National Physical Laboratory more efficient, more worthy of its name.

Increased funds must be provided, and it is only through the aid of the manufacturers, and of those who from experience have profited by the work of the Laboratory, that the Authorities can be induced to do all that is needed to establish the Laboratory in a secure position.

Recently, in the hall of the Institution of Civil Engineers, some of us listened to an address by Lord Crewe, President of the Privy Council Committee, on the subject of Industrial Research. It was in reply to a Deputation from the Joint Board of Scientific Societies. Sir J. J. Thomson, President of the Royal Society, had spoken eloquently on the claims of Pure Science, Sir Maurice Fitzmaurice dealt with Engineering, and Prof. Baker with Industrial Chemistry.

Lord Crewe announced that a large sum—the exact figure was not mentioned—is to be at the disposal of the Committee during the next five years, and outlined the scheme for its expenditure. Associations are to be formed representing various trades or industries; the representatives of these will discuss with members of the Advisory Committee, and other experts, questions needing scientific investigation, and, when these are determined, the grant, supplemented in most cases by funds raised privately or contributed by the industry, is to be used to carry them out. Such work needs laboratories, and it is here, it seems to me, that the future of the National Physical Laboratory lies. The Lord President spoke in generous terms of the work of the Laboratory in the past; its many friends who heard him were grateful for his cordial recognition of our labours, and he indicated a sphere of wider usefulness under less difficult conditions in the future. Let me picture to you what I trust that sphere may be.

In many cases, no doubt, the researches contemplated must go in special laboratories arranged and equipped for the purpose—laboratories closely connected with the industry it is desired to help, situated at the great manufacturing centres; but there are many other researches of wide interest and great importance for which a central laboratory is the proper house—a laboratory fitted and equipped in an ample manner, with a trained and competent staff animated, like those, my colleagues, who have built up the National Physical Laboratory, with a love for science, and yet withal with a keen appreciation of the practical side of the question discussed and a real desire to help our country by the application of science to industry.

The body controlling Industrial Science Research must have access to a laboratory in which may be studied the many problems which do not require for their elucidation appliances of the more specialised "works" character or opportunities only to be found in particular localities; where a staff is available, able and experienced, ready to attack under the advice of men skilled in industry the technical difficulties met in applying new discoveries on a manufacturing scale or to develop ideas which promise future success.

Such a rôle the National Physical Laboratory should be prepared to play, such is the future which I trust may be in store for it.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 7, 1916.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*The Cytomorphosis of the Marsupial Enamel-organ and its Significance in Relation to the Structure of the Completed Enamel.*" By J. T. Carter.

The marsupial enamel cell in its life cycle passes through fourteen distinct stages, the last nine of which coincide with its period of active functional life. There is a progressive differentiation of the cytoplasm into metaplasm and the formation of a fibrillar cytomitoplasm, succeeded by a period of rejuvenation in which the cytomitoplasm is probably the active factor. Associated with this rejuvenation is the degeneration and disappearance of certain cells of the stratum intermedium.

The ameloblastic secretion is shed from the ends of the ameloblasts at which surface the cytoplasm becomes modified to act as a cell membrane, and the intercellular areas are closed by the development of structures which connect these areas together.

The Tomes' processes are not cytoplasmic, but are forms assumed by the secretion, and are purely metaplasmic.

The ameloblastic secretion is at first homogeneous and forms a continuous layer, which undergoes two distinct coagulations or gel-formations. The first of these takes the form of a spongework, in the walls of which the "fibrils" arise; the lamellæ constituting the walls of this spongework eventually disappear, but the fibrils persist as the so-called "tubes" of the marsupial enamel. The alveoli of the spongework are considerably larger than the bases of the enamel rods and are occupied by a clear homogeneous coagulum. This undergoes a further coagulation which assumes the form of a honeycomb and constitutes the interprismatic material of the enamel. Calcification of the tissue is effected by adsorption of calcium into the substance of this honeycomb, which progresses until its cavities are obliterated and a solid substance results.

All structures seen in the completed enamel arise from changes in the ameloblastic secretion.

"*Development of the Pancreas, the Pancreatic and Hepatic Ducts in* Trichosurus vulpecula." By MARGARET TRIBE.

"*The Typical Form of the Cochlea and its Variations.*" By H. J. WATT.

"*Structure and Biology of Archotermopsis, together with Descriptions of New Species of Intestinal Protozoa, and General Observations on the Isoptera.*" A. D. IMMS, D.Sc.

"*Torsional Hysteresis of Mild Steel.*" By J. J. GUEST and F. C. LEA.

In this paper a series of experiments are described which show that when mild steel is subjected to a torsional reversal of stress the material does not follow Hooke's law, and that there is a distinct stress-strain hysteresis loop even for comparatively small ranges of stress.

A new and sensitive torsion machine, which can be loaded in such a way as to readily reverse the torque, and a new torsion meter capable of measuring very small strains are first described. A new method of plotting stress-strain curves, so that the hysteresis loop can be clearly shown, is described and used in connection with the paper. Hysteresis loops for varying ranges of stress are shown, and the loop obtained is shown to depend in a given cycle upon the previous history of the material.

The effect of a small overstrain on the material is investigated, especially in relation to subsequent hysteresis loops, elastic limits, and slight yields. Any small overstrain is shown to disturb the elastic properties of the steel very considerably.

The effect of time and of heating the steel at the temperature of boiling water and at higher temperatures on the hysteresis loop obtained for a given range of stress after such overstrain, is also investigated. These all, to different extents, reduce the width of the hysteresis loop and tend to restore the steel to what may be considered its natural condition.

The paper is illustrated by carefully-made drawings of hysteresis loops, obtained under various conditions, and by a perspective sketch of the machine and the torsionmeter.

MISCELLANEOUS.

Society of Chemical Industry.—Special Notice.—The Committee of the London Section propose that a series of meetings shall be held during the coming session at one of the London hotels, at which informal discussions will take place among the members. It is hoped that this departure may prove useful in promoting the good fellowship of the members, as well as in indicating new lines to be followed in increasing the utility of the Society's work. Light refreshments will be provided at these meetings at the member's expense. The first meeting was held at the Birkbeck Café, Holborn, W.C., on December 19, when a Discussion was opened by the Chairman on "The Work of the Section." In order that these meetings shall be a success, the Committee are desirous of securing as good an attendance as possible, and they particularly desire that the younger members of the Section may make an endeavour to be present, and to take part in the discussion.—THOMAS D. MORSON, Hon. Sec. and Treasurer, 14, Elm Street, Gray's Inn Road, London, W.C.

Royal Technical College, Glasgow.—The Governors, at the request of certain donors, offer prizes, amounting to £70, for essays on the "Best Methods of Training and Employing in Industries, other than Agriculture, Returned Soldiers and Sailors, Maimed or otherwise." The prizes will be awarded by a Committee of the Governors, and may be withheld in the event of no essay of sufficient merit being submitted. The decision of the Committee on this and all other points will be final. Essays must be sent in not later than March 1, 1917, addressed to the Director, the Royal Technical College, Glasgow.

Andrew Carnegie Research Scholarship Fund.—The Council of the Iron and Steel Institute is prepared to make annually from the Research Scholarship Fund, founded by Mr. Andrew Carnegie, Past-President, a limited number of grants in aid of research work on problems of practical importance relating to the metallurgy of iron and steel and allied subjects. Directors of private and public laboratories, principals of metallurgical training establishments, and managers of iron and steel works who desire to promote research work on some problem connected with the metallurgy of iron and steel or an allied subject, are invited to submit proposals for its investigation with the aid of a grant from the Carnegie Fund, and to nominate some qualified person to carry out the work under their supervision. Independent investigators are also invited to apply for a grant for similar purposes, provided that they satisfy the council that they are properly qualified to carry out the research work which they propose to perform. The value of the grant would depend on the estimate of the cost of the proposed research work, but the maximum amount which can be granted in any one year will, as a rule, not exceed £100. The payment of the grants will be made in quarterly instalments to the person performing the research work with the approval and knowledge of the person or authority under whose supervision it is being carried out. In the case of independent investigators, a brief report on the progress of the work would be required before each instalment became due. Proposals should be submitted on a special form, to be obtained from the Secretary of the Institute. The cost of publication of reports on research work would be borne by the Iron and Steel Institute, which would also have the right of priority of publication in full. The publication of reports can be deferred if good reason can be shown for not giving immediate publicity to the results of the research work. In considering the allocation of grants, the Council cannot pledge itself to accept any particular proposal, but will be guided by the nature of the subjects proposed for investigation and will give preference to those which, in their judgment, appear to be of the most practical advantage to the iron and steel and allied industries.—G. C. LLOYD, Secretary, 28, Victoria Street, London, S.W.

NOTES AND QUERIES.

⁎ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Over-Seas Club.—One of the members of this Club is anxious to know the prices ruling in the London market for Pâte de Terclenttine, Gomme Brutée, and Beta-Naphthol. We should be very obliged if any correspondent could give us this information or tell us the best place to which to apply.

MEETINGS FOR THE WEEK

THURSDAY, 28th.
SATURDAY, 30th.
Royal Institution, 3. (Christmas Lectures, anapted to a juvenile auditory). "The Human Machine which all must Work," by Prof. Arthur Keith, M.D., F.R.S., &c.

THE CHEMICAL NEWS

Vol. CXIV. No. 2979

A NEW METHOD FOR THE DETERMINATION OF VAPOUR DENSITIES.*

Part X.

By PHILIP BLACKMAN.

The need of a condenser, &c., as a heating apparatus can easily be dispensed with and a thermostatic bath be employed, which not only very much simplifies the supporting apparatus, but is especially useful in the study of dissociation by temperature of dissociating bodies. It will be found to possess another considerable advantage in that the bulb in which the body has to be vaporised can be made as large as one wishes (consistent with the size of the thermostat), and thus the quantity of mercury to measure the vapour-pressure and the length of rubber pressure-tubing to be manipulated are greatly reduced.

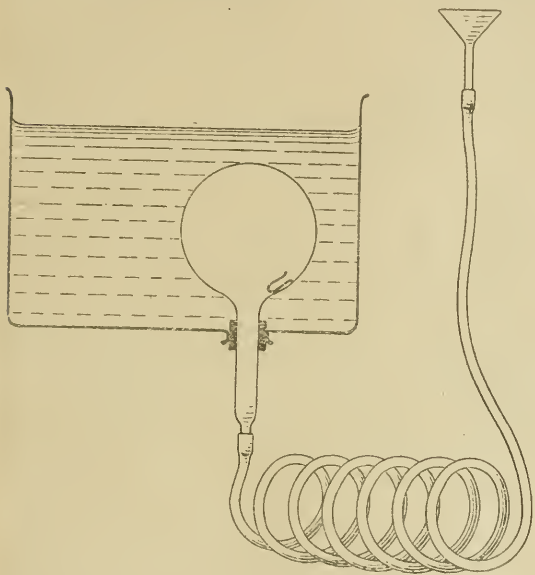

Fig. 1.

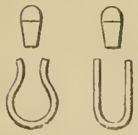

Fig. 2.

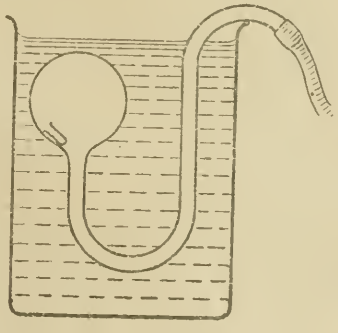

Fig. 3.

The "bulb" (Fig. 1) may be adapted from an ordinary measuring flask with a neck wide enough to admit the tiny "density" bottle containing the weighed quantity of substance to be vaporised. The neck of the bulb passes through the bottom of the thermostat. The operations are exactly the same as those described in Part IX. of the series.

Where it is undesirable or impossible to have a "neck" in the bottom of the thermostat, the "bulb" has an S-neck (Fig. 3) of sufficient internal diameter and width of bends to allow the "density" flasks (Fig. 2, approximate size) to pass in and out freely.

With this latter form of apparatus, before the heating is proceeded with the pressure should be greatly increased, to prevent the vapour or air from escaping round the shallow bend.

Before use the bulb should be cleaned and dried, and finally air blown through it by aid of a thin rubber tube.

London

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.*

The Electrolytic Determination of Cadmium in Cadmium Bromide.

By GREGORY PAUL BAXTER, MERRITT ROY GROSE and MINER LOUIS HARTMANN.

(Concluded from p. 302).

Method of Analysis.

For all the electrolyses a cell of the Form II., as shown in the earlier paper by Baxter and Hartmann, was employed. In order that the cell might be subjected as far as possible to the same influences before the initial weighing as before the final weighing, it was carefully cleaned and provided with suitable charge, usually about 100 grms. of the purest mercury, and the mercury was then made the cathode during the electrolysis of dilute sulphuric acid for several hours. Then the cell was rinsed first with water, and then with alcohol. The outside also was cleaned and wiped with a clean lintless cloth. In order to dry the cell and contents it was placed in a tubular desiccator containing fused potassium hydroxide, and the pressure was reduced as far as possible with a Geryk oil pump. When the alcohol had evaporated the cell and its counterpoise were placed in a second vacuum desiccator containing fused potassium hydroxide, and allowed to stand for several hours before being weighed.

Next the quartz boat with its content of cadmium bromide was introduced bodily into the cell, and the salt was dissolved in the rinsings of the weighing bottle. The column of bulbs to catch spray formed during electrolysis was inserted, and electrolysis was begun, usually with current strength of about one-half ampère. A strong current at the start was found to delay the completion of the electrolysis. The cell was partly immersed in the purest water in order to avoid undue heating during electrolysis. By experiment this water was proved to exert no appreciable solvent effect upon the glass of the cell.

One of the chief difficulties met in the work was the removal of the bromine liberated at the anode, which, owing to its considerable solubility, nearly all dissolved in the bromide solution, and was only slowly eliminated by evaporation into the small volume of gases produced at the electrodes. This dissolved bromine, by its action on the amalgam, greatly retarded the deposition of the cadmium. Various means of hastening the evaporation of the bromine were tried, including the addition of sulphuric acid before electrolysis was begun, varying the current strength and the concentration of the solution as well as the temperature, but the only one which was at all successful was to cause a stream of very small bubbles of pure electrolytic hydrogen to pass through the electrolyte through a small glass tube which extended nearly to the surface of the mercury. Even with this device a small amount of bromine remained in the solution after electrolysis for eighteen hours. By that time, however, nearly all the cadmium was deposited, and it was safe to remove the electrolyte and eliminate all bromine and bromide by conversion to sulphate.

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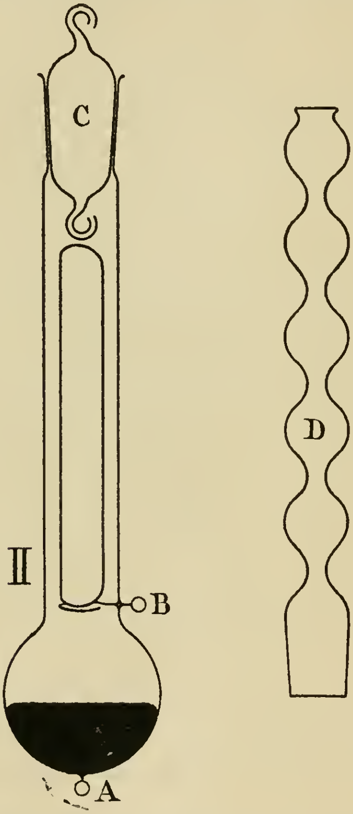
* Continued from the *Journal of Physical Chemistry*, 1911, xv., 569; Chemical News, 1910, ci., 121.

* *Journal of the American Chemical Society*, xxxviii., No. 4.

Before doing this the column of bulbs was rinsed into the cell, and the current strength was increased to a maximum by applying the full potential of the battery (17 volts) across the electrodes. Next the electrolyte was removed by suction as completely as possible, and the amalgam was washed with a few portions of water and left standing under a very dilute solution of sulphuric acid. The electrolyte was transferred to a quartz dish, and evaporated with a few drops of distilled sulphuric and nitric acids until the bromine and nitric acid had been expelled, and the sulphuric acid was fuming. The residue, which amounted to only a few mgrms., was dissolved in water and returned to the cell, and the electrolysis was continued over another period, usually of sixteen hours, with a current strength of between ½ and 1 ampère. The electrolyte was now replaced with very pure water, the full potential being maintained between the electrodes, and great care being taken not to break the electrolytic circuit. Then the water was removed as completely as possible, and the amalgam was rinsed with two small portions of chilled water which had been saturated with hydrogen, and two small portions of the purest alcohol, the amalgam being rolled round gently so as to bring the surface in thorough contact with each washing portion. The outside of the cell was then carefully cleaned and wiped dry, and the amalgam was freed from alcohol exactly as the mercury originally was treated. In accordance with the earlier experience of Baxter and Hartmann we found the amalgams to remain constant in weight when preserved in vacuum.



The electrolyte and washings were evaporated nearly to dryness in a quartz dish over an electric stove. After transference to a weighed platinum crucible evaporation was continued at a gradually increasing temperature until finally the sulphuric acid had been expelled. Eventually the residue was heated to very dull redness before being cooled and weighed. While this residue was always small, in no case was it negligible, and occasionally weighed several mgrms. After being weighed it was in many cases dissolved in very dilute sulphuric acid, and the solution tested for cadmium with hydrogen sulphide. Cadmium was always found, usually in amounts corresponding very nearly to the weight of the sulphate. Undoubtedly, however, a small proportion of the residue consisted of sulphates of alkalis extracted from the glass of the cell. Since the residue is always multiplied by the proportion of cadmium in cadmium sulphate, 0·54, before the correction is applied, no serious error could have been introduced in this way. That this is the case is indicated by the fact that the total weight of cadmium computed from amalgam and residue eventually became constant upon repeated electrolysis, while the residue seldom changed in weight materially, and frequently decreased.

In the earlier analyses the percentage of cadmium in the bromide was found to be even higher than corresponds to the atomic weight 112·42. The results for the atomic weight of cadmium varied somewhat, the highest being 112·477 and the lowest 112·387, with an average of 112·43. The amalgams, while not badly rusted, were, however, not quite so bright in appearance as in the earlier electrolyses of cadmium chloride. In Analysis 1, in the Table, in which the initial result was somewhat higher than usual, the experiment was tried of repeatedly dissolving the residue of cadmium sulphate in dilute sulphuric acid, returning it to the cell and continuing the electrolysis for another period of several hours. The result of these experiments was to diminish the total weight of cadmium found in the amalgam and residue by about 2 mgrms., the change falling chiefly upon the weight of the amalgam. Ultimately, a point was reached where repeated electrolysis produced no further alteration in the weight of cadmium recovered. These additional electrolyses, besides lowering the total weight of cadmium, also improved the appearance of the amalgam perceptibly, the final product being as bright and silvery in appearance as could be desired. While we are not certain as to the exact cause of this diminution in weight, we are strongly inclined to the belief that it is due to a small amount of mercurous bromide on the surface of the amalgam, which is only gradually reduced to the metallic state by prolonged electrolysis. This mercurous bromide might very well be formed through the action of the free bromine always present during the first stage of the electrolysis. After this experience in every analysis the residue was dissolved in dilute sulphuric acid, returned to the cell, and the electrolysis repeated until the cadmium recovered in the form of amalgam and as sulphate reached a constant minimum value. This required from three to five electrolyses. The ultimate result of this change in procedure was to lower slightly the average percentage of cadmium in the bromide from that obtained in the first series of experiments.

In order to make certain that the final weight of cadmium found in this way is the correct one, two experiments, Analyses 10 and 11, were carried out by converting the bromide completely to sulphate before electrolysis was begun. This is the method employed by Quinn and Hulett for the analysis of cadmium bromide. The boat with the fused salt was transferred to the quartz dish, and the salt was dissolved in water. The boat was carefully removed with rinsing, and the solution was slowly evaporated on an electric stove with a slight excess of

The Atomic Weight of Cadmium. (*a*)

Cd : Br_2. Br = 79·916.

Number of analysis.	Sample of $CdBr_2$	Weight of $CdBr_2$ in vacuum. Grms.	Weight of Cd from amalgam in vacuum. Grms.	Weight of residue from electrolyte. Grm.	Total of Cd in vacuum Grms.	Ratio Cd : Br_2.	Atomic weight of Cd.
1	A	16·55663	6·83505	0·00133	6·83575	0·703203	112·395
2	B	6·83764	2·82293	0·00090	2·82342	0·703355	112·419
3	A	7·16223	2·95618	0·00144	2·95696	0·703155	112·387
4	B	6·71886	2·77347	0·00124	2·77414	0·703255	112·402
5	C	10·31855	4·26065	0·00087	4·26112	0·703453	112·434
6	C	9·40020	3·88027	0·00213	3·88142	0·703311	112·412
7	C	8·21123	3·38976	0·00115	3·39038	0·703274	112·406
8	C	10·51504	4·33980	0·00323	4·34154	0·703254	112·403
9	C	10·22411	4·22110	0·00087	4·22157	0·703297	112·409
10	C	10·99613	4·53953	0·00112	4·54013	0·703242	112·401
11	C	11·05166	4·56258	0·00109	4·56317	0·703271	112·405
12	D	19·67134	8·12101	0·00266	8·12244	0·703309	112·411
	Average	.. .. ..	.. .. ..	.. .. ..	.. .. ..	0·703282	112·407
	Total ..	127·66362			52·71204	0·703281	112·407

Cd : Cl_2. Cl = 35·457.

		$CdCl_2$.				Cd : Cl_2.	
13		6·49746	3·98314	0·00216	3·98430	1·58537	112·425
14		6·62682	4·06323	0·00047	4·06348	1·58523	112·415
15		7·35812	4·51120	0·00084	4·51165	1·58500	112·399
	Average	.. .. ..	.. .. ..	.. .. ..	.. .. ..	1·58520	112·413
	Total ..	20·48240			12·55943	1·58519	112·412

(*a*) Some of the preliminary analyses of cadmium bromide were made by Dr. Hartmann. The final analyses given in the tables were all made by Mr. Grose.

re-distilled sulphuric and nitric acids until the bromine and excess of nitric acid had been expelled. The greatest pains was taken toward the end of the evaporation to avoid spattering. The residue of cadmium sulphate and sulphuric acid was dissolved in water, and the solution quantitatively transferred to the cell and electrolysed. The amalgam was treated as above preparatory to weighing, and the residual electrolyte was evaporated in quartz and finally in a platinum crucible, and the residue of sulphate was weighed. The residue was dissolved in dilute sulphuric acid, returned to the cell, and electrolysis was repeated. In Analysis 10 the change in weight when electrolysis was repeated was 0·01 mgrm. In Analysis 11 during the first repetition the loss was 1 mgrm., owing apparently to the fact that some undecomposed bromide was left in the sulphate, but in the second repetition a gain of 0·06 mgrm. occurred. The agreement of the results of these two experiments with those of experiments where the bromide was electrolysed directly is strong evidence that no serious error affected the latter.

A question raised by the gradual loss in weight of the cadmium amalgam during continued electrolysis of the bromide is whether in the earlier analyses of cadmium chloride a similar process might have not been under way but not detected. Therefore, in order to determine whether in the analysis of the chloride it is necessary to continue electrolysis to constant weight, several experiments were carried out in as nearly as possible the same fashion as in the work by Baxter and Hartmann, except that the residue was dissolved, returned to the cell, and electrolysis repeated one or more times after the initial weight had been obtained. The material was made from Sample C of cadmium bromide used in the present work by converting it to chloride in a stream of chlorine and hydrochloric acid. The latter process was carried out exactly as described in the earlier paper on the analysis of the chloride (Baxter and Hartmann, *loc. cit.*, p. 130). In no one of the three analyses in which electrolysis was repeated could a change in the total weight of cadmium as large as a 0·1 mgrm. be detected. One analysis in which an obvious loss of material occurred is not given in the table. The final average of the three determinations is essentially the same as that found before. We therefore feel reassured that no difficulty such as was experienced with the bromide could have affected the chloride analyses. It is not surprising to find this to be the case, however, since the free chlorine, being more volatile and less soluble in the electrolyte, is far more rapidly removed during electrolysis than the free bromine.

The weights were standardised to hundredths of a mgrm. by the substitution method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144). All weighings were made upon a No. 10 Troemner balance. With the heavier objects, such as the weighing bottle, and the cell containing mercury or amalgam, the balance beam was left down some minutes before making observations in order to allow the slight bending of the beam to occur. A small amount of crude radium bromide was kept in the balance case to prevent the objects weighed from retaining electrostatic charges. The weighing bottle and cell were always compared with counterpoises of very nearly the same shape, size, and volume in order to avoid variations from changes in atmospheric conditions.

Vacuum corrections of +0·000086 grm. per grm. of cadmium bromide and of +0·000152 grm. per grm. of cadmium chloride were applied, the densities of the weights and the salts being assumed to be 8·3, 5·192, and 4·047, respectively. The vacuum correction of cadmium dissolved in mercury computed in the earlier paper, −0·000016 grm., was applied for every apparent grm. of dissolved cadmium. In a few analyses the amalgam was so concentrated that a small amount of solid amalgam separated, but not in amount large enough to produce uncertainty in the vacuum correction.

One analysis is omitted from the table of bromide experiments because the stopper blew out of the cell during the drying of the amalgam, and one because of the presence of a relatively large amount of readily volatile solid residue when the electrolyte was evaporated to dryness. The amalgam in Analysis 2 was re-electrolysed only once, and lost in the process 0·00062 grm. This may account for the fact that the result of this experiment is slightly higher than the average. In Analysis 7 constant weight of the cadmium was not secured because of accident to the residue after the third electrolysis. In the second electrolysis the loss in weight was 0·00055 grm.; in the third 0·00024 grm. It is unlikely that an appreciable further loss would have occurred. In Analysis 5 a very slight black ring, presumably of mercury sulphide, formed on the glass of the cell at the surface of the mercury during the electrolysis with sulphuric acid.

In connection with the table it is worth noting that if the weight of residue obtained from the electrolyte is entirely neglected, the atomic weight of cadmium becomes 112·37. But this value is surely too low, first, because the residues always contained cadmium, and, second, because of material dissolved from the cell walls.

The average result, 112·407, confirms all the earlier work in the Harvard laboratories upon the analysis of the cadmium halides. The average percentage of cadmium in cadmium bromide found here is 41·290, while Baxter, Hines, and Frevert by comparing the same salt with silver found the percentage of bromine to be 58·708. The sum is 99·998 per cent, a satisfactory outcome.

The following table summarises the work upon the atomic weight of cadmium carried out in the Harvard laboratories:—

	Ratio.	Atomic weight of cadmium.
Baxter and Hines ..	$CdCl_2 : 2Ag : 2AgCl$	112·418
Baxter, Hines, and Frevert	$CdBr_2 : 2Ag : 2AgBr$	112·417
Baxter and Hartmann	$CdCl_2 : Cd$	112·417
Baxter, Grose, and Hartmann	$CdBr_2 : Cd$	112·407
	Average..	112·415

It is difficult to believe that constant errors could have affected all four series of results to an equal extent.

Summary.

1. A procedure for the direct electrolysis of bromides with the use of a special form of cell and a mercury cathode is described.

2. Further evidence is presented in support of the analyses of cadmium chloride by Baxter and Hartmann.

3. The percentage of cadmium in anhydrous cadmium bromide is found to be 41·290, while Quinn and Hulett found only 41·257 per cent. The former percentage corresponds to an atomic weight of cadmium of 112·407 ($Br = 79·916$), a value which agrees satisfactorily with the results obtained earlier by Baxter, Hines, and Frevert, and Baxter and Hartmann, 112·417 ($Cl = 35·457$). The average of the four series of results is 112·415 ($Ag = 107·880$).

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance in this investigation.

Technological Examinations.—The report on the examinations for the current year of the City and Guilds Institute has just been published. Like all other examining bodies, the Institute has suffered seriously in the numbers of its candidates during the past two years. In 1913-14 there were altogether 23,119 who came up for examination. Last year this number dropped to 15,623, and this year to 8508. There was also a falling-off in the number of centres: this year there were 316, last year 419, and the year before 467. The record year seems to have been 1910, when 24,508 were examined at 418 centres. The number of subjects of examination has now reached 79, a considerable development of the 14 which the Society handed over to the Institute in the year 1879.—*Journ. Roy. Soc. Arts.*

ON A PRECISION METHOD OF UNITING OPTICAL GLASS.

THE UNION OF GLASS IN OPTICAL CONTACT BY HEAT TREATMENT.*

By R. G. PARKER, B.Sc., A.C.G.I., and A. J. DALLADAY.

Owing to the numerous defects of the cements available for constructing glass cells for the examination of the optical properties of liquids, the following process, by which a much more perfect joint between two pieces of glass can be obtained, has been developed. Briefly, the surfaces of each of two pieces of glass are so worked and polished that they are either both plane or of the same curvature to a very high degree of accuracy. They can then be placed together in "optical contact," and if they are subjected to carefully controlled heating will unite and become one piece.

In order that this method may be of any value, it is essential that the temperature at which union takes place shall not only be far below the melting-point of the glass, but also below the annealing temperature - for even at this temperature very slight strain would cause sufficient deformation of worked glass surfaces to render them useless.

It is very difficult to place the windows of a cemented cell sufficiently accurately parallel for certain work depending on the phenomena of the interference of light; parallelism to ± 1 (one) minute is only attained with considerable trouble, especially if the adhesive material requires baking to cause it to harden completely. The wedge shape of the enclosed liquid may be too great for interference work, even if the angle between the windows is not greater than a few seconds.

In addition, cements frequently strain the materials which they hold together to such an extent that their optical properties are considerably altered. The interference rings are produced between the plate and a proof-plane of quartz; the plate was originally very flat, and showed less than one interference ring across its entire face. After cementing, the series of rings appeared, indicating a depression in the centre of the plate of about 1/5000 in. There appears to be considerable force acting radially inwards; such distortion would render the glass plate useless for almost any accurate optical instrument, especially if polarised light were passed through it or interference phenomena were being observed.

Glass surfaces can be polished without difficulty so nearly flat—or so nearly of the same curvature—that when carefully cleaned and freed from dust, they show less than one interference fringe per inch when placed together and examined by light reflected from the interfaces. Such surfaces can be pressed into optical contact by the application of pressure of several pounds per square inch, and the pieces of glass act as one for optical purposes—for example, if the hypotenuse of a 45° prism is in such contact with another piece of glass, no total reflection—indeed, no reflection at all—is obtained from the common surface. They can easily be separated by sudden warming or cooling, by force, if applied in a *peeling* manner, and by liquids; the latter gradually creep in and lift the surfaces apart. The joint is very resistant to forces tending to slide one surface over the other.

A cell constructed of two plates of glass in optical contact with a U-shaped separating piece would have the advantages of great accuracy of parallelism between the windows; very little strain in the windows if the components were of one kind of glass and put together at the same temperature, and an "all glass" construction, involving no cement to contaminate liquids placed therein, and to perish eventually under the action of solvents or corrosive substances. But it would be quite useless, owing to the ease with which such surfaces can be separated by the methods described above.

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* A Paper read before the Faraday Society, December 18, 1916.

It is well known that if glass is heated it gradually becomes less viscous as the temperature rises, passing through all degrees of viscosity until at a high temperature it is quite mobile; there is thus no sharp melting-point, but only an approximate position which varies from about 1100—1400° C. At temperatures very much below the melting-point the glass is still liquid enough to deform gradually under stress—hence the slow permanent bending of a glass rod supported at each end, in a horizontal position, and at ordinary temperatures. Glass behaves, in fact, as a brittle elastic solid under sudden strain, but as a viscous liquid to severe strain applied over long periods when at ordinary or moderately elevated temperatures; with rise of temperature the elastic nature of the glass becomes more and more masked by the decrease in viscosity, and at a temperature approximating to the melting-point it becomes no longer observable.

Annealing Temperature.—If a piece of glass having two plane, parallel, and polished sides is placed in an electric furnace so that it can be heated, and examined by transmitted polarised light at the same time, the strain caused by unequal heating can be observed both as regards position and intensity by its effect on the light. This strain, which would be very evident at lower temperatures in a piece of glass in the form of a ½-in. cube or larger, suddenly disappears over quite a short range of temperature situated very much below the melting-point. The glass has obviously reached a temperature at which it is sufficiently mobile to accommodate itself rapidly to the stresses caused by unequal heating; it is therefore deformed, and the stress disappears; this is clearly the annealing-point, in that a piece of badly annealed glass would lose all internal stress at this temperature, and if sufficiently slowly cooled would be perfectly annealed.

Relation of the Temperature employed to the Annealing Temperature.—The viscosity of a glass at its annealing temperature is still very great, but it has softened sufficiently for a pointed tool, pressed against it with considerable force, to make its way slowly in. Therefore, an optically worked surface of a piece of glass would not retain its form accurately after heating to the annealing temperature, if some clamping apparatus had touched the surface.

The mobility of glass has been found to be an exponential function of the temperature—

$$S_T = S_{T_1} A^{\frac{T - T_1}{N}}$$

where S_T, S_{T_1} are the "mobilities" at the temperatures T, T_1, measured by the rate of deformation of glass under constant stress, and A and N are constants for the glass. The quantity N is comparatively small, so that for quite small values of $T - T_1$ the index $\frac{T - T_1}{N}$ would become equal to 1, 2, 3. . . . If, for example, we take $N = 8$, $A = 2$, and compare the values of the mobility of the particular glass at temperatures of $T = 560°$ C. and $T_1 = 552°$ C., 544°, 536° successively, we find the respective values of the mobility to be—

$$\begin{aligned}\frac{S_T}{S_{T_1}} &= 2^1 && \text{when } T_1 = 552° \text{ C.}\\ &= 2^2 = 4 && \text{when } T_1 = 544° \text{ C.}\\ &= 2^3 = 8 && \text{when } T_1 = 536° \text{ C.}\end{aligned}$$

That is, the glass becomes twice as "soft" for *every* rise of temperature of 8° C. Therefore, at 60° or 70° C. below the annealing temperature a glass has become sufficiently hard to withstand very great local pressure for short periods without sensible deformation. The method of determining the annealing temperature will be described at a later date; it should be known accurately for each kind of glass which is to be joined, as by this means only can we obtain a sufficient welding effect together with the minimum risk of injury to the surfaces.

Working at this temperature, 60° C. below the annealing-point, two pieces of glass under pressure, and in optical contact, will unite perfectly in less than one hour. At the same time the deformation of the outer surfaces caused by the imperfections in the plates compressing them is so very slight that a few strokes on a polishing tool are all that is necessary to restore them to the condition of optical surfaces of high accuracy; or treatment of the surfaces may be altogether unnecessary. It is, perhaps, well in practice to work at a temperature 10—20° below this maximum safe temperature in order to ensure that no deformation shall occur.

Methods of Distinguishing between Optical Contact and Complete Union.—With regard to tests for distinguishing perfect union, we have already noted that the optical contact of two surfaces is easily destroyed by sudden temperature change, by the action of liquids, and by mechanical force; when the contact has changed into complete union, they cannot be separated by any of these means, and if force is used the two pieces of glass break as one —not along the interface. A crack or a diamond cut spreads through the two pieces as though one piece of glass, whereas if the pieces are merely in ordinary optical contact, it cannot be made to pass from one to the other.

Experimental.

The temperatures selected for our experiments on the union of glass surfaces was considerably below the annealing-point, in accordance with the facts already discussed. Two preliminary experiments were made, using a metal box having 7-in. sides, filled with sand, and heated by gas burners. Pieces of crown glass, 5 × 5 × 1·5 mm., were put into contact, wrapped in asbestos wool, and held together by a clamp; they were then heated at the rate of 1° C. per minute to a probable maximum of 400—450° C., maintained at this temperature for one hour, and slowly cooled.

They were found to have united, but not completely. When torn apart with considerable force each piece carried with it glass from the other. All the surfaces were optically perfect after heating.

In the second experiment larger pieces (1 in. dia., ¼ in. thick) of different kinds of glass were employed—crown and heavy flint. Heating was as before, but rather more vigorous; probable maximum temperature 450—500° C. The glass was clamped between pieces of brass plate, with asbestos packing. The discs united at one place only; here the joining was perfect, and when they were forced apart the flint carried with it a portion of the crown over the whole of this area. The external surface of the flint glass was spoiled, as it had softened slightly; the crown glass was almost uninjured.

These experiments having proved that joining would take place, more careful ones were conducted with a view to constructing apparatus by the method.

A platinum-wound electric tube furnace (internal dimensions of the oval tube 3½ in. × 2½ in., 14 in. long) was fitted with double silica windows at each end. It was controlled by two resistances in series. One, the main resistance, was used to compensate for the very great changes in the resistance of platinum which take place between 20° C. and 600° C.; the second permitted of much more gradual changes of resistance, and formed the fine adjustment in this respect. The temperature at any instant was known by means of a platinum resistance thermometer, allowance being made for any lag in its indications, and, further, the thermometer was connected to a Callendar recorder, giving a permanent record of the temperatures used in any experiment, and enabling the *rate of change* of temperature to be seen at a glance.

The heating and cooling were therefore very completely under control, and a continuous temperature change as small as ¼° C. per minute could be maintained indefinitely.

An arrangement by which polarised light could be passed through the furnace, and examined after passing through the piece of glass or silica under test, completed the apparatus. By this means the effect of unequal heating caused by rise or fall of temperature could be observed, and if necessary the actual stresses set up in any part of the test-piece could be calculated at any time during or after the experiment.

Three plates, all of a hard crown glass, were put into optical contact, the centre one being about 10 mm. thick, and drilled so as to give a cell suitable for the comparison of two liquids, as in the Rayleigh interference refractometer. The outer plates were, of course, merely windows of about 3 mm. thickness. The cell was heated without pressure in the electric furnace at the rate of 2° C. per minute to 460° C., and after two hours at this temperature it was cooled at 4—5° C. per minute; the arrangement of the furnace permitted continuous inspection of the cell. During heating, at 200—300° C., minute imperfections in the contact grew rapidly, one side of the cell coming almost completely away. When cold it was found to be out of contact over parts of the surface, the rest of the surface being in contact, but covered in spots.

Rapid temperature changes, such as would easily have separated glass in ordinary contact, had no effect; water also failed to lift the surfaces apart, and when a thin knife-blade was forced in from a corner where the two surfaces were apart, that portion of the window out of contact was broken off without moving the window as a whole. The cell was then compressed in a vice in such a way as to apply large shearing stresses at the interfaces, with the result that corners of the windows out of contact broke away, while the rest in contact remained unchanged.

The spots referred to above were small round areas where the surfaces were just out of contact. Each developed from a minute flaw in the optical contact of the surfaces, and when examined microscopically very minute black particles could be seen in each, and from the system of Newton's rings apparent in them during the heating they appeared to contain a gas at high pressure; by the same means the pressure was observed to diminish slowly after a spot had spread outwards to one edge of the cell, and finally (in a later experiment), when the temperature was raised above the annealing-point, the walls of each spot were slightly but definitely blown out, so as to appear convex from the outside. It therefore appears that the spots are due to the decomposition of minute particles of cellulose from the rag used in cleaning the surfaces; a pressure of many atmospheres can be produced in this way. By careful cleaning it is possible to eliminate them almost entirely. Cells which have comparatively large areas in contact are less free from spots than those in which no point is far from an edge; the gases which would remain permanently enclosed in the former are able to escape from the latter, and the surfaces then go back into complete contact.

The optical surfaces of this cell were found to be perfect and quite unchanged after heating, including the unsupported internal surfaces; we therefore have *optically worked* surfaces in the *interior* of a solid glass cell. It is not well known that ground-glass surfaces act as if they were in compression; thus, a thin plate originally flat and polished on both sides becomes, when finely ground on one side, a concave mirror of long focus on the other. In the case of our cell, the rough surfaces of the drilled holes push up a burr round the edge which is only a few wave-lengths high, but sufficient to prevent complete optical contact. This burr was therefore removed by "retouching" on a polisher, but traces of it evidently remained, and by producing local pressure caused the union to be very complete over its surface. Severe strain was applied by forcing a thin wedge between the two surfaces without breaking this narrow area of complete union. The same effect was also shown by another corner of the same cell which was out of contact after heating and was broken off; the fracture travelled round the edge of the drilled hole instead of passing straight across it.

A second cell was then made of the same glass and pattern, and heated at the rate of 1—1½° C. per minute to a temperature nearer the annealing-point—523° C.—at which it was kept for two hours, then cooled at 4—5° C. per minute. Pressure was applied by means of a hand screw-clamp. Two brass plates, with surfaces ground flat, and sufficiently thick to eliminate bending (¼ in. thick), were used to distribute the pressure; a few thicknesses of thin paper were placed between the brass surface and glass surface to take up minute irregularities; the carbonisation of the paper did not interfere with its action.

The union of the three components was complete except for a few small spots. They could not be separated by any of the means indicated, and when subjected to severe mechanical strain a portion of the cell broke away, showing the conchoidal fracture of a solid glass block. No bending of the fracture occurred at the interfaces, except at one small portion where a spot showed that there was no contact.

The optical surfaces had all remained perfect as regards plastic deformation. The outer surfaces were slightly corroded by the paper ash, and had to be repolished. When examined by means of a Babinet compensator (for the effect on polarised light), very little internal stress was observed, in spite of the unnecessarily rapid cooling; the maximum stress indicated was about 150 lbs. per square inch. This amount could easily be decreased, but is already negligible for most purposes.

A third cell of rather different construction showed very few imperfections of contact. Heating was carried out exactly as in the previous case; *i.e.*, at 90° C. below the annealing-point. The areas in contact are all narrow, and no point is more than 2½ mm. from an edge. Any centres of gas pressure developed in the way already described are therefore likely to disappear owing to escape of the gas, and we find, in general, that these narrow areas give the most perfect joining.

The glass of the cell showed very little strain, although no special precautions, such as annealing, were taken. By avoiding temperature differences when putting the components into optical contact, and by subsequent slow cooling from the annealing temperature, all traces of strain can be eliminated.

The internal surfaces of the cell windows were parallel to one second both before and after union. The degree of parallelism remained quite unaltered, and it therefore appears that the accuracy of parallelism is determined only by the initial accuracy of the central component.

Union of Two Different Kinds of Glass.—The components of the cells described above were all made of one kind of glass, and the joining of different glasses is complicated by at least three factors—differing expansion coefficients, differing annealing points of the glasses, and the degree of ease with which they will fuse together in the blowpipe flame. The first will certainly cause the surfaces to come apart while the temperature is rising, but if they are under pressure at about 30 lb. per square inch this should not greatly matter, as they will go into contact when the temperature is constant at its highest limit, and they will then join perfectly. Strain will appear owing to different contraction as they cool, now as one piece, but for some purposes it may not matter. Such strain as this cannot be obviated by "annealing." Difference in the annealing points is the more exacting factor, for unless the annealing-points of the glasses to be joined are fairly close (within perhaps 50° C.) the more fusible one will reach its annealing-point before the less fusible reaches a temperature at which it will unite with another glass in any reasonable time. The annealing-points of glasses in common use may differ by 200° C. or even 250° C., and it is obvious therefore that many pairs of glasses could be selected which would be very difficult or impossible to join; on the other hand, for most purposes suitable glasses can be chosen. With regard to the last factor, it appears that certain kinds of glass which will not fuse together readily in the blowpipe flame will also not unite by the new method.

A Rayleigh cell prepared of hard crown glass with plate-glass windows was heated to a low temperature—400° C.—at the rate of 2—2½° C. per minute and kept at the maximum temperature for one and a half hours. Pressure was not applied. In consequence of this, and also of the different temperature expansion coefficients, they remained in optical contact only over a very small part of the surfaces. When cold the glass was found to have united in these places in spite of the unnecessarily low temperature. The areas of contact were so small that the windows could be forced off without fracture and they then carried with them glass from the other component. The optical surfaces had not been changed by the heating.

This experiment (as well as that described above) indicated that two glasses of quite widely differing annealing points could be joined even under unfavourable conditions.

A more severe test was then carried out with an object-glass having curves of the same radius on the common faces of its components. The annealing-points of the two glasses employed (flint and crown glass) differ so widely, it was thought advisable to heat approximately to the annealing temperature of the softer glass. The lenses, in optical contact, were clamped together at the edge at three equidistant points, then heated at 1—1½° C. per minute to a maximum temperature of 476° C. They remained so for one hour and then cooled at 4° C. per minute. They were then completely out of contact, except under the three points at which pressure had been applied; in these places there was perfect union. The flint lens had softened to such an extent that slight dents had been made in its surface by the clamp. Both lenses were found to be strained when examined by polarised light. A few spots which had developed in the usual way from minute dust particles had blown out into flat bubbles in the flint glass, indicating that they contained gas under great pressure, as we had already inferred.

It appears, therefore, that the flint and crown glasses commonly used in object-glasses differ too widely in annealing temperatures for successful union. Owing to the large number of factors which limit the nature of the glasses to be employed, this is one of the most difficult cases to which the method has been applied.

Polarimeter Tubes.—A polarimeter tube having windows permanently fixed in position by this method was prepared without difficulty. The tube was of soda-lime glass and the windows of plate-glass; maximum temperature 470° C. The joint was perfect, and in spite of the fact that different glasses were employed the windows showed little strain—the amount was found not sufficient to interfere with measurements of rotation in any way. For many purposes this form of tube should be very convenient, especially in respect of ease of cleaning and freedom from corrosion. As soon as possible we intend to apply this construction to jacketed tubes; they would somewhat resemble the ordinary pattern of glass Liebig condenser, and should, with careful heating, withstand very high temperatures. The nature of the hot circulating liquid would be determined only by the temperature required, and not by the powers of resistance of the cement, as is the case at present.

Union of Fused Silica.—An experiment with component parts of this material showed that there was no essential difference between its behaviour and that of glass; the temperature required for union was naturally found to be much higher. The upper limit of temperature to which silica glass apparatus may be heated is determined by its power of devitrifying; this takes place at about 1200—1300° C. (Blackie, *Trans. Faraday Soc.*, 1911, vii., 158; Crookes, *Proc. Roy. Soc.*, 1912, A, 86, 406) and is accompanied by great decrease in mechanical strength. It is obvious that a very small amount of devitrification would be sufficient to spoil silica glass for optical work, especially as it takes place more readily where there is access to the air, *i.e.*, at the surfaces. The highest temperature which we can use is therefore somewhat below 1200° C.; fortunately, a preliminary experiment has shown that a still lower temperature will suffice.

The annealing temperature of silica was not determined, as the small temperature expansion coefficient and good heat conductivity rendered it somewhat difficult to produce observable strain by heating, in the small pieces of transparent silica which were available.

Two plates of silica glass 0·75 × 0·5 × 0·1 in. were put into optical contact with the ends of a silica ring 1·0 in. dia. and 0·5 in. long, in order to make a small cell suitable for investigating the ultra-violet absorption spectra of liquids. This was held in a steel clamp, wtth a few thicknesses of paper inserted between the steel and the silica, and heated to 1030° C. for one hour.

While cooling, contraction of the clamp fractured the cell, but portions of it, examined when cold, were found to have joined. On forcing them apart some of the material of the plate was torn away by that of the ring, and *vice versa*; from the nature of the union we judge that a rather higher temperature, probably in the neighbourhood of 1100° C., will be required to give results equal to those attained with glass. The planeness of the silica plates was found to be unchanged.

In conclusion, we wish to thank Mr. F. Twyman, of Messrs. Adam Hilger, Ltd., for continued help and many suggestions.

FEDERATION OF BRITISH INDUSTRIES.

Recommendations for the Development of the Government Service for the Promotion of British Trade in Foreign Countries.

The Federation of British Industries has had under consideration the circumstances which will affect British foreign trade on the conclusion of peace and the preparations necessary to meet the new situation, and they desire to urge the following views upon the earnest attention of His Majesty's Government.

It appears inevitable that economic conditions after the war, and more particularly those which will exist in belligerent countries, will greatly increase the severity of the competition in foreign markets at the very time that the necessity of meeting the heavy charges consequent upon war expenditure will render it a vital necessity for British productions to secure a greatly increased sale in such markets.

This situation will involve a great increase of effort upon the part of all persons, organisations, and individuals concerned with the industry and commerce of the country; but, above all, a very heavy responsibility will be thrown upon the Government Commercial Service, and, in particular upon the departments and services charged with the promotion of foreign trade and with the collection and distribution of foreign commercial intelligence. The Federation are convinced that these responsibilities will be of such a nature that the duties, character, and scope of these departments and services will require radical reorganisation and a very considerable extension.

They fully realise, however, that it is not within the power of any Committee to lay down detail reforms, and they have therefore confined themselves to suggesting certain broad principles which in their opinion are essential to any successful reorganisation.

Concentration of Control in a Single Department.

In the first place they consider that in any organisation of the immense size and scope required for the Government Commercial Service, where the action of individual officers, however able, is necessarily limited by the regulations, spirit, and character of the whole service, the adoption of a system based upon sound principles of organisation is a question of the first importance.

They feel, therefore, that any mere attempt to impose detail reform or additions upon the existing organisation will be doomed to failure, and that the only chance of success lies in a fundamental reconstruction of the present administration.

The first essential in any sound system of large scale organisation is the provision of an active, vigorous, and homogeneous central control, and the Federation believe that such a control can only be obtained by the concentration of the entire responsibility for the appointment and promotion of the personnel of the service, and for the direction of all their duties, in the hands of a single department, which shall also be in the closest possible touch with the industrial and commercial community, and responsible both for the distribution to them of the information collected, and for ascertaining from them their needs and wishes in relation to foreign trade.

Their first recommendation, therefore, is that a single department shall be selected, and that this department shall be charged with *all* duties connected with the promotion of British trade in foreign countries, and with such duties at home as are necessary to enable it to be in close and constant touch with the industrial and commercial community, and to direct the services abroad with a full and first-hand knowledge of industrial and commercial problems and necessities.

Selection of Controlling Department.

The next question of principle in laying down the bases of a sound reconstruction, is the selection of the department which is to exercise this control.

In considering this question, the Federation desire to suggest that the reconstruction required is of so fundamental a character, and will involve so complete a reorganisation of any department selected, that it is unnecessary to attach much weight to the relative fitness or unfitness for the task of existing departments or of their personnel, and that the main object to be kept in view is the selection of a department whose natural functions are, or should be, of a character best adapted to harmonise with those of a department charged with the duty of promoting British trade in foreign countries.

Judged from this standpoint, the Federation believe that the only department which it is possible to charge with these duties is the department in general charge of Foreign Affairs.

They have reached this conclusion principally because they are convinced that foreign commercial policy can only be successfully conducted as an integral and most important part of general foreign policy, and that it can never be so conducted unless the responsibility for the conduct of both policies is concentrated in the same department.

Industrial and commercial interests are the most vital factor in the relations between modern States, and the primary cause of the existence of such relations, consequently the successful conduct of foreign policy in all its branches depends upon a due realisation, both in theory and practice, of the close inter-dependence and interaction of political and economic motives.

Such a realisation can never be attained by men who are not accustomed to deal with both political and commercial questions as part of their ordinary duties, and any system which deprives the department and service charged with the conduct of foreign affairs of full opportunities of gaining knowledge and experience of industrial and commercial questions will inevitably lead, as it has led in the past, not only to a failure to allow due consideration and importance to these questions, but also to serious errors of proportion and consistency in the general foreign policy of the country.

In addition to this argument, which appears to the Federation to be in itself conclusive, it must be considered that the only alternative to the step suggested is to create a new Commercial Foreign Service under the direction of some other department.

Such a course is virtually impossible owing to the practical and international difficulties surrounding the establishment on a large scale in any foreign country of a Government service which is not under the direct control of the department responsible for the conduct of general relations with that country.

Any attempt to avoid these difficulties either by dividing the home control of such a service between two departments, or by leaving the home direction of the service under one department and placing the personnel abroad under the nominal control of His Majesty's representatives, who are themselves responsible to another department, will re-introduce in a peculiarly vicious form the dual element which has already been shown to be incompatible with sound organisation.

Finally, it seems probable that the large questions involved by railway, loan, dock, and similar projects, and by the majority of schemes for the development of the natural resources of foreign countries, will assume a greatly increased importance in the future.

These questions, which not only contain a strong political element, but also as a rule involve direct negotiations with the Government of the country concerned, must, together with the negotiations arising from the general readjustment of international commercial relations after the war, and the large range of problems of a nature partly political and partly commercial raised by the resolutions of the Paris Conference, necessarily remain for the most part in the hands of the department and service dealing with Foreign Affairs.

Nothing but the most disastrous consequences can be anticipated if this department and service is not in the most intimate and direct touch with industrial and commercial opinion, and is not afforded the fullest possible opportunities of extending and improving its knowledge and experience of industrial and commercial questions.

The Federation, therefore, desires as its second Recommendation to urge as strongly as possible that the only department which can be charged with the promotion of British trade in foreign countries is the Foreign Office.

Functions to be Fulfilled by this Department.

It next becomes necessary to outline broadly the functions which should be allotted to this department and to the Foreign service; to define in general terms the division between its sphere and that of the department in general charge of commercial and industrial affairs; and, finally, to suggest the general principles upon which the Federation consider that the detailed reorganisation of the department and service should be based.

In the first place, then, the Federation consider that the Foreign Office should be responsible for the protection and promotion of all British industrial, commercial, and financial interests and activities in foreign countries, and for the collection and distribution of all information on matters connected with industry, commerce, or finance in those countries.

These duties should include the prompt and vigorous support of all British efforts to secure contracts, concessions, or orders in such countries. This support may—and indeed, to secure success, should—at times entail the selection of one of several British competitors.

The issue of all foreign loans in the United Kingdom should be subject to the approval of His Majesty's Government, and a necessary condition of such approval should be that the larger portion of the goods or services purchased by such a loan should be obtained from British sources.

In all cases support should only be accorded to *bona fide* British firms, and should be refused to all firms, whether technically British or not, which are in any degree under foreign influence.

The Federation are aware that these proposals involve an extension of the sphere of activities previously considered suitable for a Government service and a possible interference with the liberty of action of individual firms, but they consider that this extension is fully justified by the paramount necessity under present circumstances of securing the greatest possible increase of the earning power of British industry and the maximum of employment for British workers.

Functions left to the Department in Charge of General Commercial Matters.

The functions outlined above leave to be found means for the necessary organisation and control of industrial and commercial activity at home, and the collection of commercial intelligence respecting the Dominions and Crown Colonies.

The Federation are of opinion that these functions should pertain to the department in general charge of commercial affairs, whether this department is the Commercial Section of the Board of Trade, a Ministry of Commerce, or any other department.

They believe, however, that it is essential that really efficient machinery should be established for the co-ordination of the work of the Foreign Office and of this department, and that in home industrial, commercial, or financial matters which may affect or be affected by the course of foreign trade, the latter department should consult the Foreign Office freely and fully, and should be to a large extent guided by its advice.

They also consider that all items of commercial intelligence, whether collected by the Foreign Office, Board of Trade, or any other department, from any part of the Empire or the world, should be made immediately accessible to the other departments, and that, at least in so far as the Board of Trade and Foreign Office are concerned, a complete record of all the commercial intelligence in the possession of His Majesty's Government should be available in each department.

Reorganisation of Foreign Office and Foreign Services.

It is obvious that this division of functions, together with the necessity for a great increase in the scope, and a marked improvement in the performance, of the duties in connection with foreign trade, will necessitate a reorganisation and extension of the Foreign Office and of the Foreign Services, and a considerable reform both of their methods and personnel.

Funds.

The first essential to such an extension and reorganisation is a considerable increase in the funds allotted for the conduct of these services.

In this connection the Federation desire to state that they consider that an adequate expenditure on the Foreign Commercial Service is as necessary as an adequate expenditure on National Defence.

Granted the necessary preliminary in the shape of adequate funds, the Federation desire to make the following general recommendations with regard to the organisation of the Foreign Office and of the Diplomatic, Consular, and Commercial Attaché Services.

Foreign Office and Diplomatic Service.

With respect to the Foreign Office, they would recommend the establishment of a large Commercial Branch to undertake the duties which have been outlined above, and the provision of extra staff and accommodation for this branch upon a generous scale.

The members of this branch should be placed in all respects—service rank, emoluments, and future prospects—on a footing of absolute equality with the members of the Political Branch, and there should be a constant mutual exchange of officials, at any rate in the junior ranks. In fact, every effort should be made not only to promote the closest possible co-operation between the two branches, but to establish the fact that service in the Commercial Branch is fully as important and as likely to lead to professional advancement as service in the Political Branch.

The Federation consider that it is of the most vital importance that the Commercial Branch should be in the closest possible touch with the industrial and commercial community. They therefore recommend that the officers of the branch should, as part of their regular duties, be available for personal interviews with British subjects who desire to discuss foreign trade questions and that they should pay frequent visits to industrial centres.

In addition to these facilities for personal intercourse they would recommend that small committees should be selected, representative of the manufacturing, commercial, and financial firms interested in the trade of the countries dealt with by each section of the Commercial Branch.

These committees should not merely act as consultative bodies for the sections, but should be encouraged to make suggestions and criticisms relating to the general conduct of commercial policy in the spheres for which the various sections are responsible.

In addition to these Sectional Committees, a Central Committee should be established to advise the Foreign Office and Board of Trade on questions of general commercial policy, to suggest the initiation of new policy, and to criticise where necessary the manner in which policy already decided upon is being carried out. Leading members of the industrial and commercial community should form a large and important element on this Committee.

With respect to the Diplomatic Service they would propose the increase of the Diplomatic and clerical staffs at all Embassies and Legations to the extent necessary to enable Diplomatists to devote a considerable portion of their time to the study of industrial and commercial questions and to the acquisition of practical experience in dealing with them.

In regard to the personnel of the Foreign Office and Diplomatic Service, the Federation consider it a matter of the greatest importance that all members of these services should possess sufficient knowledge, and should acquire sufficient practical experience, to enable them to judge the value and importance of the commercial factors in any general problem with which they may be dealing, and they therefore suggest that a certain minimum of commercial experience in each grade of the service should be rigidly insisted upon as a qualification for promotion to the next grade, such experience to be gained by work at a Consulate, by work with the Commercial Attaché, by work in the Commercial Branch of the Foreign Office, by a combination of these means, or by direct experience.

Commercial Counsellors.

It is obvious, however, that the members of the Diplomatic Service, although they should realise that industrial and commercial questions form a regular and most important part of their work, and that it is their duty to devote at least as much time and attention to these as to purely political questions, will, from the conditions of their service, seldom, if ever, remain sufficiently long in any one country to acquire a detailed and expert knowledge of local industrial and commercial conditions.

The Federation would therefore recommend that, in order to supply this local knowledge, and the necessary continuity of local commercial policy, the present Commercial Attaché should be replaced by an officer of high rank attached to every Embassy and Legation, who might be entitled the Commercial Counsellor.

This officer should be given a rank, position, and emoluments second only to those of the Ambassador or Minister, to whom he should act as expert adviser in all questions affecting, or likely to be affected by, industrial or commercial considerations.

He should also have sole charge of all the commercial work in the country, including all necessary powers of inspection and supervision, and in all commercial matters his authority should be second only to that of His Majesty's representative, to whom he should be responsible.

Immediately under this officer should be one or more assistants, according to the size and commercial importance of the country, whose headquarters should be placed at the most important commercial centres.

Both the Commercial Counsellor and his assistants should be given opportunities of paying frequent visits to the United Kingdom, in order that they may consult commercial interests, and keep in touch with the latest developments in industry and commerce.

The members of this service should be provided with ample travelling allowances to enable then to cover their districts thoroughly, sufficiently high emoluments to secure a first-class personnel, suitable office accommodation where required, and efficient clerical assistance.

While Commercial Counsellers and their assistants should remain as long as possible in one country in order to permit of their acquiring a thorough knowledge of local conditions, influences, and personalities, they should form an integral portion of the general Diplomatic Service, and promotion to the highest posts in that service should be open to such of them as show marked ability.

Consular Service.

The members of the regular Consular Service whose commercial duties will, as previously stated, be subject to the direction of the Commercial Counsellor, should be largely increased, in order to enable them to fulfil these duties adequately, and their emoluments, prospects, and conditions of service should be improved in order that men of first-rate ability should be attracted to the service.

This increase in numbers should be accompanied by an extensive redistribution of posts to correspond more closely with commercial needs than the present distribution, by the reduction to a minimum of the number of posts held by unpaid officers, who should not in any case be entrusted with other than purely routine Consular duties, and by the provision of more suitable premises at the numerous Consulates which are at present inadequately and inconveniently housed.

At the same time Consular officers should be provided with sufficient clerical and other assistance to set them free from all but a general supervision of routine Consular duties, and to enable them to devote the bulk of their time and energies to commercial work, and the whole scale of local and travelling allowances should be revised in order that the Consuls may travel freely in their districts, and may take a sufficiently prominent part in the social and official life of their posts to ensure their meeting local commercial men of importance on equal terms.

General Recommendations with respect to the Recruiting, Promotion, and Training of all Services.

Recruiting.—The Federation are of opinion that only natural born British subjects should be eligible for appointment to any position, paid or unpaid, in the foreign service of the country, and would recommend that this should be made a definite rule which should not be broken on any pretext. The creation of the new Commercial Branch of the Foreign Office will necessitate a considerable increase of staff, and they consider that it is of importance that this opportunity should be taken to introduce a leaven of practical commercial experience, which should be of particular value in the early days of the new branch when its procedure and methods are being established and its traditions formed. With respect to the Commercial Counsellors and to the Consular Service, they consider that men of ability should be selected whenever they can be found, and—as in the case of the Commercial Branch of the Foreign Office—they attach great importance to the introduction of men of practical business experience in the early stages in order that a sound business tradition may be established. They realise that the work of a public service is essentially different from that of a private business, in that it is necessarily general rather than specialised in character, and that the officers of such a service, whatever their original occupation, will tend to be moulded by the character and conditions of their work rather than by any influences which may have been brought to bear upon them prior to their appointment. They consider, however, that it should always be possible to find a few men of commercial experience who are particularly qualified for this work and attracted by it, and they consider that a small but constant flow of fresh blood from this source should be invaluable, as providing a means of keeping the general spirit and character of the service in harmony with commercial views and objects.

Promotion.—It seems obvious that the bulk of the services, to whatever extent they may or may not be recruited from men of actual business experience, will consist, in fact, of men who have always been, or who have become as a result of their work, permanent officials in character and outlook, and it therefore becomes doubly necessary to provide such a powerful stimulus in the work itself and in the rewards for it, and so close a touch with the industrial and commercial community, that this outlook is as near to that of a man engaged in promoting his own business as is possible and desirable. The Federation believe that it would be impossible to provide this stimulus by any system of bonus or payment by results which would not be so manifestly inequitable as to do more harm by rousing discontent and jealousy in the service than it did good by stimulating zeal. They recommend, therefore, that the necessary stimulus should be provided in all the services and in the Foreign Office by the institution of a definite standard of efficiency, which must be reached by all officers at certain stages of their career. This standard should be a very high one, and should be administered by a Promotion Board, of which the membership should be sufficiently large to exclude any risk of personal prejudice influencing the decisions. This Board should be given power to postpone the promotion of all officers who fail to reach the required standard, and to enforce the resignation of officers who fall far below it. As a corollary to this power, and as a condition essential to its adequate employment, the Board should also be permitted to grant pensions, commensurate with their past services, to all officers who are called upon to resign, whether these officers have reached the present pensionable age or not. The Federation would be glad to see some such system adopted for all Government service, but they feel that it is a question of peculiar importance in a service in which energy, initiative, and enthusiasm are such vital factors, and where the influence of the man who has done good work in the past, but is now serving on for his pension, without hope and without interest, is so particularly disastrous, not only to the duties upon which he is actually engaged, but to the efficiency and character of his subordinates and successors.

Training.—As it is impossible, and indeed undesirable, for officers who must be prepared to assist any of the infinitely varied industrial or commercial activities in which a British subject may indulge, to become specialists in any particular branch, it is obvious that any training must be of a general rather than of a special character. The essential qualifications, therefore, are those of character and general education, and the Federation would suggest that the preliminary examination for the selection of candidates should be as far as possible of a type calculated to test general ability and a sound general education. As, however, knowledge of commercial methods, even if it is only theoretical, should be of considerable value in enabling an officer to grasp more rapidly the practical requirements of his work, and their relation to other factors, the Federation would recommend that the candidates for *all Services*, either before or after appointment, should be required to pass a general course in elementary economics and commercial method, such as those now provided by the faculties of several of the universities; with this course should be incorporated a study of two or more foreign languages. The remainder of any officer's training must be acquired, as in all other professions, by the actual performance of his work, but the Federation would recommend that frequent opportunities should be given to the officers of all services to pay visits to industrial centres, and that every effort should be made to render these visits as instructive as possible. They consider it of great importance that officers should in all cases possess an intimate knowledge of the language of the country in which they reside. The Federation would be glad to offer any assistance in their power to promote the practical commercial training of candidates for, or members of, the foreign services, and hope shortly to be able to put forward some concrete proposals for the consideration of His Majesty's Government.

Provision of a Staff of Experts.

As the knowledge and experience of the officers of the regular services must be general in character, it will become necessary to provide means for securing detailed and expert reports on particular trades, industries, or markets.

The Federation would therefore recommend that a large number of commercial and technical experts should be selected and employed on temporary missions, as and when required, to investigate and report upon industrial or commercial conditions or opportunities in particular markets and particular countries. These experts should be paid a fee for each investigation sufficiently large to ensure that the best possible advice is obtained, and ample funds should be provided to secure that these investigations can be made with sufficient frequency and thoroughness.

In conclusion, the Federation would urge most strongly upon His Majesty's Government the vital importance of taking immediate steps to reorganise the service, in order that the conclusion of peace may not find the country unprepared to face the serious industrial and commercial competition in foreign countries which must be an inevitable consequence of the war.

The reorganisation and development of the personnel and methods of this service must necessarily be a work demanding considerable time, and it is the realisation of the disastrous consequences which may ensue if this work is not undertaken at once which has impelled the Federation to put forward these Recommendations immediately, without incurring even the short delay which would have been necessitated by awaiting the completion of their investigation into the problems of trade with the Dominious and Colonies, which will, however, be submitted to His Majesty's Government in due course.

ROYAL AGRICULTURAL SOCIETY OF ENGLAND.

War Emergency Committee's Suggestions.

Mr. R. Prothero, President of the Board of Agriculture, attended the first meeting of the War Emergency Committee of the Royal Agricultural Society of England, under the Chairmanship of Mr. Adeane. He outlined the Government's proposals for increasing the production of food, and after his departure the Committee passed the following resolutions, which are being forwarded to the Board of Agriculture:—

1. That this Committee is of opinion that a price should not be fixed for any agricultural produce unless cost of production is taken into consideration and unless the price of feeding stuffs, fertilisers, &c., is also fixed. The Committee questions the wisdom of fixing prices, but in the event of the price of wheat being at 60s. per quarter, the opinion of the Committee is that the price of oats should be fixed at not less than 40s. per quarter.
2. The Committee is of opinion that where Spring sowing of wheat is undertaken, care should be taken to ensure that the varieties used should be especially suitable for the purpose—such as Red Marvel, April Bearded, or, in districts where it is known to succeed, Red Fife.
3. The Committee feel that the land of this country cannot be made to produce more food unless there be an increase in the supply and use of artificial manures. The manufacturer of these manures is dependent upon a larger amount of sulphuric acid being made available for the use of the makers of artificial manures, and the Committee urge the Government to set free for the use of those manufacturers such acid as they may require.
4. The Committee are of opinion that in view of the great difficulty experienced in obtaining artificial manures in this country, the Government be requested to prohibit the export of sulphate of ammonia and basic slag, except to our Colonies, until the requirements of agriculturists of this country have been met.
5. This Committee views with the gravest apprehension any proposal to send for sale in England horses cast from the Army in France. They are of opinion that it would be a most unwise proceeding to import these horses having regard to the grave risk of introducing and spreading disease. This Committee requests the President of the Board of Agriculture to safeguard the farmers interests in this matter, both now and at the end of the war.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 6, 1916.

Mr. George Embrey, President, in the Chair.

A certificate was read for the first time in favour of Prof. Alfred Francis Joseph, D.Sc., F.I.C.

A certificate was read for the second time in favour of Mr. Gerrard W. Baker.

The following papers were read:—

"*Brazilian Oil Seeds.*" By E. Richards Bolton, F.I.C., and Dorothy G. Hewer, B.Sc.

The authors drew attention to the importance of utilising all the available sources of supply of fats and oils for edible purposes, as well as for soap and glycerin manufacture, and they go on to show why certain oleaginous products, known to yield large quantities of oil, have been neglected in the past.

They refer to the vast supply of oleaginous seeds in Brazil, and of these the palms are of the greatest economic importance, as all those mentioned yield a kernel oil which can be rendered edible, leaving a non-fatty residue of value as a cattle food.

Analytical and botanical data were given for the seeds and fruits of the following:—

1. *Palms.*—A Brazilian variety of the African palm (*Elæis guineensis*), Tucum, Murumuru, Paraguay palm, Ansja, Piririma, Babassu, and Pataua.
2. *Various Seeds.*—Ucuhuba, Myristica platyspermum, Paroa-caxy, Maboula Panza, Sacha Almendras, Marins, Mamurana, and Mahuba-rana.

"*Copying-ink Pencils and the Examination of their Pigment in Writing.*" By C. A. Mitchell, M.A., F.I.C.

Synopsis.—Composition of the Pigment; Methods of Examination; Variations in the Products of Different Makers; Reactions of the Pigments in Writing; Identification of Pigment; Colour Comparison; Osborn's Colour Microscope; Differential Tests; Cases of Rex *v.* Wood and Rex *v.* Seddon; Permanency of the Pigment; Experiments *re* SS. *Merbland* (Macbeth *v.* King)—Was the vessel torpedoed?

"*The Analysis of Honey and other Substances containing Fructose.*" By W. R. G. Atkins, Sc.D.

The paper deals with a suggested method of estimating

			0			I.	II.			III.	IV.		V.	V.	VII.
H = 1	2	3	He 4	5	6	Li 7	8	Gl 9	10	B 11	C 12	13	N 14	15	O 16
17	18	F 19	Ne 20	21	22	Na 23	Mg 4	25	26	Al 27	Si 28	29	30	P 31	S 32
33	34	Cl 35	36	37	38	K 39	Ca 40								
										Al_2O =	Si_2O =				
										Ga 70	Ge 72				

NOTE.—The position of F 19 would seem to suggest an ancestral 3—the ideal halogen (!); that of Mg 24 presupposes a lost 8; and that of P 31, a lost 15.

the sugar usually found in ordinary honey by oxidation with bromine of the aldehydic glucose, which leaves untouched the ketonic fructose. This fructose may then be determined separately by the usual polarimetric or reduction methods, giving thus a direct determination of one of the sugars instead of the usual—and, probably in the case of such a sugar, the less accurate—method of indirect estimation by the solution of two simultaneous equations.

"*Military Sanitation.*" By Capt. C. G. MOOR, F.I.C.

SOCIETY OF CHEMICAL INDUSTRY.
(NEW YORK SECTION).

A MEETING of the Section was held in Rumford Hall, 50, East Forty-first Street, New York, on November 24, 1916.

The programme for the evening included an Address by the Chairman, JEROME ALEXANDER, on "*The Importance of 'Impurities.'*"

After directing attention to the possibility of potent action by very small percentages of substances, a number of instances are mentioned wherein so-called impurities, previously neglected, have proven to be of prime importance.

In conclusion, it is pointed out that no factor in research or technical practice should be disregarded, no matter how insignificant it may seem, or however lowly the source of information.

"*Some Present-day Techno chemical Problems.*" By RAYMOND F. BACON.

In this address there are suggested a large number of research problems to be solved in the fields of metallurgical problems to be solved in the fields of metallurgical, industrial inorganic, and industrial organic chemistry. Particular attention is given to those problems which could be advantageously attacked outside of industrial plants, especially in the laboratories of our universities. The address therefore includes a consideration of the methods which might be employed for the establishment of stable relations between industrialists and institutions having facilities for conducting investigations of the type indicated.

CORRESPONDENCE.

A REVISION OF THE PERIODIC TABLE.

To the Editor of the Chemical News.

SIR,—Probably many of your readers and correspondents would be interested in the enclosed problem.

If the numerals from 1 to 40 are placed in their natural order, when we select those which correspond with the atomic weights we shall find there is always a jump of 16 from one element to its next below.

If we accept this order of the numerals, can we avoid the conclusion that all the elements over 16 are really irreducible compound radicals?—I am, &c.,

GORDON HARGRAVE.

Wayn Gap, Heaves, Kendal.

ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS for November 17 (vol. cxiv., p. 239) Mr. J. A. Cashmore gives a method for estimating manganese, wherein he precipitates his Mn with ammonia after oxidising the iron-free solution with ammonium persulphate. A very important point here is the purity of the persulphate. On testing the method it was found to give results about 0·1 per cent too high. This was traced to impurities of SiO_2, Fe_2O_3, &c., in the persulphate. The ordinary "pure" salt, as supplied by dealers in reagents, appears to almost invariably contain some impurities—tests giving results in the neighbourhood of 6 mgrms. of residue insoluble in HCl (presumably SiO_2), and 8 mgrms. of $Fe_2O_3+Al_2O_3$, with traces of the alkaline earths, on a 5-grm. sample.

It would be of interest and utility if Mr. Cashmore would give his experience of the method as applied to high chrome steels.—I am, &c.,

C. T. NESBITT, A.R.S.M.

Sheffield.

THE LAW OF CRYSTALLISATION OF MIXED SALTS.

To the Editor of the Chemical News.

SIR,—It is generally regarded that solutions of mixed salts are formed according to Dalton's Law of Partial Pressures as applied to vapours and gases.

In the crystallisation of mixed salts the evidenee gathered by experimenting with sodium phosphate, $Na_2HPO_4,12Aq$, containing sodium sulphate, $Na_2SO_4,10Aq$, as impurity gave the following data:—

With a 78 per cent solution of sodium phosphate, containing 5 per cent sodium sulphate, the first crystals of sodium phosphate contained 5 per cent sodium sulphate. At the end of the crystallisation, crystals of sodium phosphate containing 30 per cent sodium sulphate were obtained; the solution then containing 11 per cent sodium phosphate and 5 per cent sodium sulphate.—I am, &c.,

J. C. THOMLINSON, B.Sc.

15, Denmark Street, Gateshead-on-Tyne,
December 18, 1916.

MEETINGS FOR THE WEEK

TUESDAY, Jan. 2nd.
THURSDAY, " 4th.
SATURDAY, " 6th.
Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "The Human Machine which all must Work," by Prof. Arthur Keith, M.D., F.R.S., &c.

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